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THE ALTITUDE EFFECT ON THE SPECIFIC IONIZING POWER AND ZENITH ANGLE DISTRIBUTION OF COSMIC RAYS[1]

BY DAROL K. FROMAN[2] AND J. C. STEARNS[3]

Abstract

Measurements made with a quadruple-coincidence Geiger-Müller counting system at altitudes of 120 and 14,160 ft. give the intensity, J, of cosmic ray ionizing particles at various zenith angles, ψ. The distribution, $J_{(\psi)} = J_0 \, e^{-0.175\psi} \cos^2 \psi$, does not differ significantly from any measured values, and agrees with all observations within 0.5 and 3.0% of the vertical intensities at the lower and higher altitudes respectively. The total number of rays incident per unit area per unit time was found, and the specific ionization was determined by comparison with ionization chamber measurements. The results are given below.

Altitude, ft.	120	14,160
Mean specific ionization in ion pairs per centimetre in air at one atmosphere, i.	†54.8 ± 1.8 *82.0 ± 2.6	*87.5 ± 6
Total number of rays incident per hour per square centimetre of level surface, N_1.	78.3 ± 2.5	306 ± 22
Total number of rays incident per hour per square centimetre of surface normal to the rays, N_2.	109 ± 3.5	425 ± 30
Number of vertical rays incident per hour per square centimetre per unit solid angle, J_0.	58.4 ± 1.9	228 ± 15

† *Ionization chamber data from Clay and Jongen (4).*

* *Ionization chamber data from Millikan and Cameron (18).*

Introduction

The variation of cosmic ray intensity with zenith angle has been measured at single altitudes by Tuwim (23), Bernardini (2), Medicus (15), Skobelzyn (20), and others. Johnson (7) has made these measurements at altitudes of 620 and 6280 ft. in northern United States, and at sea level and at 14,200 ft. in Peru (8). Street and Woodward (21) have made an absolute measurement of the vertical intensity at sea level. With the aid of Johnson's measurements and Millikan's (17) ionization chamber values, Street and Woodward calculated the average specific ionization of the cosmic rays. General agreement has not been obtained on the value of the specific ionization, nor on

the variation of the zenith angle distribution with altitude.   For these reasons it was decided to redetermine the zenith angle distribution and specific ionization near sea level and at a high altitude.   Observations were made at Ste. Anne de Bellevue, Que., and at the High Altitude Laboratory on Mount Evans, Colorado.

Experimental Arrangement

The apparatus consisted of a quadruple-coincidence Geiger-Müller "telescope" with the counters arranged as shown in Fig. 1.   The counters were mounted so that the central, or direction, line (dotted in Fig. 1) could be held at any desired zenith angle, the long axes of the counters remaining horizontal. The distance, L, between the axes of extreme counters was 30.48 cm., and the inside diameter of the cylindrical electrodes in the counters was 2.54 cm.
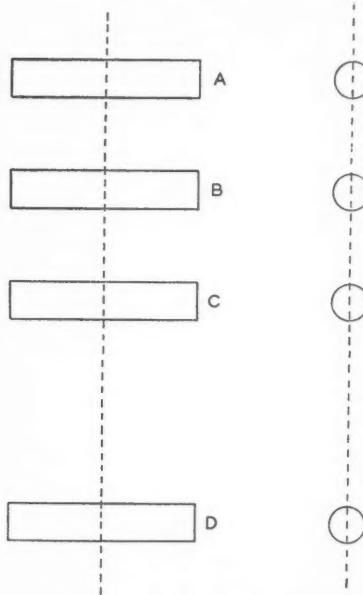
FIG. 1.   *Arrangement of Geiger-Müller counters.*

The quadruple-coincidence counting rate, *i.e.*, the frequency with which the four counters were excited simultaneously, was determined at each 15° interval in zenith angle from the vertical to 75° inclusive.   The readings were taken in the magnetic southern azimuth so as to average out the east-west asymmetry of about 2%.   The north-south asymmetry is negligible at the latitudes at which this work was done.   At the low altitude station, where the variations in barometric pressure were appreciable, a second quadruple-coincidence telescope was operated always in the vertical position.   This set furnished data for direct comparison of the intensity at any angle with the vertical intensity determined under identical meteorological conditions.

The efficiency of each counter was determined by the ratio of the quadruple to the triple counting rate with the particular counter disconnected.   In this case the counter occupied either position B or C in Fig. 1, these two positions giving the same results.   Both triple and quadruple rates were corrected for the accidental rates.   These accidental rates were determined by taking counting rates with the counters out of line.

The absorption of a counter and its shield was found by a comparison of the triple counting rates of the other three counters with the fourth counter in, and out of, line with the other counters of the telescope.

The recording circuit used was a modification of that described by Johnson and Street (10).

Theory for Determining the Absolute Intensity

Let $J_{(\psi)}$, the absolute intensity of the radiation, be the number of rays incident per unit time per unit solid angle per unit area normal to the rays at zenith angle ψ. In Fig. 2 let the z-axis be vertical and let the direction line of the counters (dotted in Fig. 2) lie in the xz-plane. The rotation of the
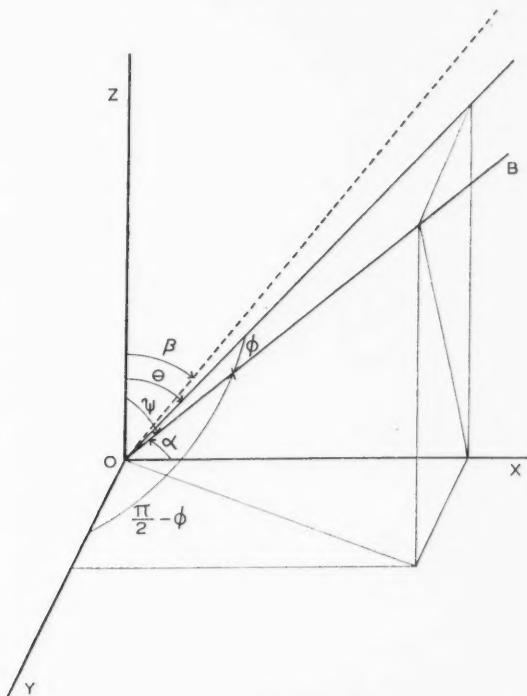
FIG. 2. *Diagram showing angular relations to aid in integration over the counters.*

system takes place about the y-axis which is parallel to the long axes of the counters. β is the zenith angle of the direction line of the counters, and the direction angles of any ray, *BO*, incident at the origin are α, $(\pi/2 - \phi)$, ψ. θ is the angle between the z-axis and the plane defined by the y-axis and the incident ray, *BO*.

Then, from Fig. 2,

$$\cos \psi = \cos \theta \cos \phi . \tag{1}$$

The side and end views of the outside pair of counters are shown in Fig. 3. From this diagram it is seen that, if we neglect for the moment the half ellipses on the ends of one extreme counter as seen from the other, the exposed

area of the counter system, projected normally to BO, is

$$
\begin{aligned}
A &= (d - L \tan \phi)\{w - L \tan |\theta - \beta|\} \cos \phi \cos |\theta - \beta| \\
&= L^2 (\tan b - \tan \phi)\{\tan a - \tan |\theta - \beta|\} \cos \phi \cos |\theta - \beta| .
\end{aligned} \tag{2}
$$
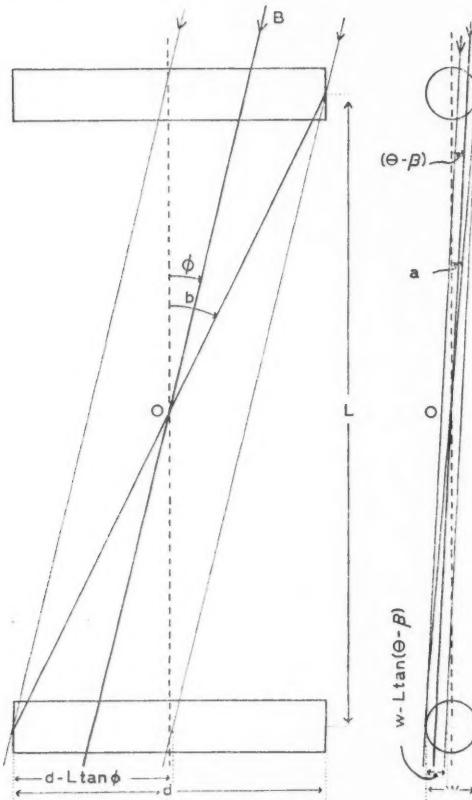
FIG. 3. *Diagram showing rays through extreme counters.*

The area is projected normally to the ray BO since the intensity, J, is defined in terms of the number of rays incident upon unit area measured normal to the rays.

Now it is known from the work of Skobelzyn (20), Johnson (7), and others that, approximately,

$$
J_{(\psi)} = J_0 \cos^2 \psi = J_0 \cos^2 \theta \cos^2 \phi, \tag{3}
$$

and this function can be used for integration over the small solid angle of the counter system for any value of β. Let $R_{(\beta)}$ be the counting rate when

the zenith angle of the direction line of the telescope is β. The solid angle contained between θ and $\theta + d\theta$, ϕ and $\phi + d\phi$ is $\cos \phi \, d\theta d\phi$. Then

$$R_{(\beta)} = \int_{\phi=-b}^{+b} \int_{\theta=-a}^{+a} J_0 \cos^2 \theta \cos^2 \phi \, . \, L^2(\tan b - \tan \phi)\{\tan a$$
$$- \tan |\theta - \beta|\} \cos |\theta - \beta| \cos^2 \phi \, d\theta d\phi \, .$$

Since the east-west asymmetry is small for the range of azimuth angle included by the counters, the ϕ-function in the integrand may be considered as even between the limits $-b$ and $+b$, and we may write,

$$R_{(\beta)} = 2J_0 L^2 \int_0^b (\cos^4 \phi \tan b - \cos^3 \phi \sin \phi) d\phi \int_{\beta-a}^{\beta+a} \cos^2 \theta \cos |\beta - \theta|$$
$$\{\tan a - \tan |\beta - \theta|\} \, d\theta$$

$$= \frac{2J_0 L^2}{\cos a \cos b} \int_0^b (\cos^4 \phi \sin b - \cos^3 \phi \sin \phi \cos b) d\phi$$

$$\times \left[\int_{\beta-a}^{\beta} \{\sin a \cos^2 \theta \cos (\beta - \theta) - \cos a \cos^2 \theta \sin (\beta - \theta)\} d\theta \right.$$

$$+ \left. \int_{\beta}^{\beta+a} \{\sin a \cos^2 \theta \cos (\theta - \beta) - \cos a \cos^2 \theta \sin (\theta - \beta)\} d\theta \right]$$

$$= \frac{2J_0 L^2}{3 \cos a \cos b} \left[\frac{3}{8} b \sin b + \frac{1}{4} \sin b \sin 2b + \frac{1}{32} \sin b \sin 4b + \frac{1}{4} \cos^5 b \right.$$
$$\left. - \frac{1}{4} \cos b \right] \left[2 (1 - \cos a)^2 + 2 (\cos a - \cos 2a) \cos^2 \beta \right], \quad (4)$$

where

$$b = \tan^{-1} d/L \quad \text{and} \quad a = \sin^{-1} w/L \, . \tag{5}$$

Street and Woodward (21) have shown the effective diameter, w, of a counter to be the inside diameter of the cylindrical copper electrode. The effective axial length, d_1, was determined by taking counting rates for various displacements of one of the middle pair of counters parallel to its long axis. Then $\frac{1}{2}d_1$ is the displacement necessary to reduce the counting rate to one-half its maximum value. However, it can be seen from Fig. 4 that, for a ray incident at an angle α to the direction line of the telescope, the effective area of an extreme counter is increased at each end by an amount

$$A = \frac{\pi r^2 \tan \alpha}{2} \, ,$$

or the effective half-length by

$$\frac{\pi r \tan \alpha}{2} \, .$$
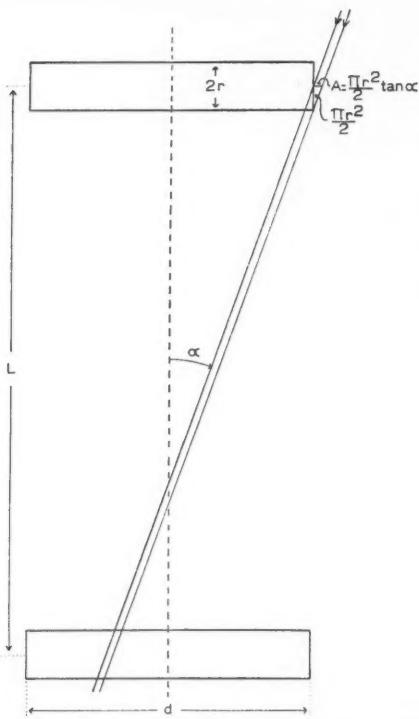
FIG. 4.   *Diagram showing end correction for extreme counters.*

Hence the mean correction to be added to the value of the effective axial half-length is

$$s = \frac{1}{\tan^{-1} d_1/L} \int_0^{\tan^{-1} d_1/L} \frac{\pi r}{2} \tan \alpha \, d\alpha$$

$$= - \frac{\pi r}{2 \tan^{-1} d_1/L} (\log_e \cos \tan^{-1} d_1/L) , \tag{6}$$

and the corrected effective length becomes

$$d = 2(d_1 + s) . \tag{7}$$

Values of $\frac{R_{(\beta)}}{J_0}$, calculated by means of Equations (4) and (5) from experimentally determined values of d, L, and w, are shown in the third column of Table I.   The use of Equation (4) means that we are assuming a $\cos^2 \psi$ distribution of intensities.

TABLE I

$\beta°$	$\cos^2 \beta$	$R_{(\beta)}/J_0$	$R_{(\beta)}/J_0 \cos^2 \beta$	$R_{(\beta)}/J_0$, corrected
0	1	1.0470	1.047	1.0470
15	0.93300	0.9769	1.047	0.9332
30	0.75000	0.7853	1.047	0.7166
45	0.50000	0.5241	1.047	0.4568
60	0.25000	0.2627	1.050	0.2187
75	0.06699	0.07122	1.062	0.05664

It will be seen from column four of Table I that $R_{(\beta)}$ is closely proportional to $\cos^2\beta$, there being only a slight deviation from proportionality at large zenith angles where the intensity is low. Hence, even if the actual intensity distribution differs slightly from a $\cos^2\psi$ distribution, β can be interchanged with ψ in any experimentally determined intensity function of β.

Let the true intensity function be

$$J_{(\psi)} = J_0 f_{(\psi)} = J_0 f_{(\beta)} . \tag{8}$$

The proportionality constants in column four of Table I are found on the assumption that $f_{(\psi)} = \cos^2\psi$. In order to find J_0 accurately from measured values of $R_{(\beta)}$, these constants must be corrected by multiplying them by $\dfrac{f_{(\beta)}}{\cos^2 \beta}$, where $f_{(\beta)}$ is the function found by experiment. The corrected values of this ratio, $R_{(\beta)}/J_0$, are given in the last column of Table I for the function

$$J_{(\psi)} = J_0 e^{-0.175\psi} \cos^2\psi,$$

which is shown later to fit the data. Thus a value of J_0 can be found from the counting rate taken at any zenith angle.

If E is the efficiency of the counting system, then the values of $J_{(\psi)}$ found by the above method must be multiplied by $\dfrac{1}{E}$ to give absolute values. Moreover, there is a correction for the absorption of the counters themselves and their shields.

The total number of rays incident per unit time per unit area of level surface will be

$$N_1 = 2\pi \int_0^{\pi/2} J_{(\psi)} \sin \psi \cos \psi \, d\psi , \tag{9}$$

and the total number of rays incident per unit time per unit area of surface normal to the rays will be

$$N_2 = 2\pi \int_0^{\pi/2} J_{(\psi)} \sin \psi \, d\psi . \tag{10}$$

If these cosmic ray ionizing particles form Q pairs of ions per unit volume per unit time in air at one atmosphere pressure, the mean specific ionization is given by

$$i = Q/N_2 \text{ ion pairs per cm.} \tag{11}$$

In calculating i by means of this relation, Q is found by ionization chamber measurements, and it is assumed that only the ionizing rays which actuate counters are responsible for the ionization.

Experimental Results

Observations of the cosmic ray intensities were made continuously from September 28, 1936 until June 3, 1937, at Ste. Anne de Bellevue, and from July 1 until July 15, 1937, at the Mount Evans High Altitude Laboratory.

The efficiency of each counter was measured at each station.   The efficiency, E, of the system is the product of the separate efficiencies of the four counters. Table II gives the accidental counting rates and efficiencies.   The efficiencies of all four counters were nearly the same.

TABLE II

Altitude, ft.	120	14,160
Triple accidental rate per hr.	0.6 ± 0.1	3.3 ± 1.0
Quadruple accidental rate per hr.	0.3 ± 0.08	0.7 ± 0.3
Efficiency of quadruple set, E	0.833 ± 0.021	0.515 ± 0.036

The effective axial length, d_1, was found by taking counting rates for various displacements of one of the middle counters.   These rates, less accidentals, at an altitude of 120 ft. are given in Table III, and are plotted against displacement in Fig. 5.   From Fig. 5, the value of half of the effective axial length is found to be 5.96 cm., *i.e.*, $d_1 = 11.92 \pm 0.05$ cm.   The probable error given for d_1 is estimated from the probable errors given in Table III.
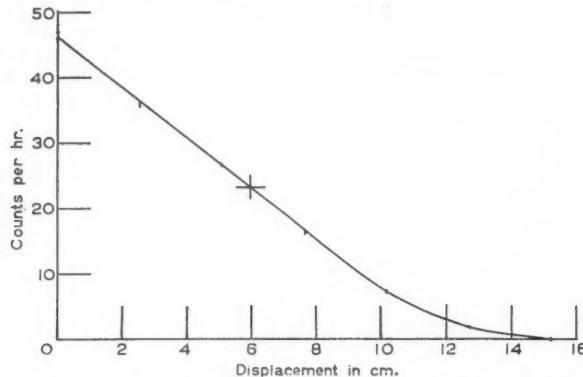
FIG. 5.   *The variation of counting rate with lengthwise displacement of a middle counter.*

The observed counting rates, $R_{(\beta)}$, at the two stations are given in Table IV. These values are corrected for accidentals, but are not corrected for efficiencies and absorption of the counters. The values for altitude 120 ft. have been corrected to a barometric pressure of 76.0 cm., and those for altitude 14,160 ft. to a pressure of 46.7 cm. These pressures are very near the means at the two stations and the corrections are small.

TABLE III

Displacement in cm.	Counting rate per hr.
0.00	46.5 ± 0.38
2.54	35.9 ± 0.42
5.08	26.9 ± 0.36
7.62	16.44 ± 0.28
10.16	7.73 ± 0.18
12.70	1.82 ± 0.11
15.24	0.00 ± 0.08

TABLE IV

$\beta°$	Altitude 120 ft.		Altitude 14,160 ft.	
	Total counts	$R_{(\beta)}$ per hr.	Total counts	$R_{(\beta)}$ per hr.
0	48360	44.4 ± 0.14	4706	106.6 ± 1.0
15	20605	39.9 ± 0.19	2058	92.3 ± 1.5
30	15743	30.7 ± 0.16	1359	76.0 ± 1.3
45	9742	19.0 ± 0.14	1109	43.9 ± 0.9
60	4573	8.90 ± 0.09	506	24.3 ± 0.6
75	1579	2.51 ± 0.05	255	7.6 ± 0.4

The counting rates given in Table IV are plotted against zenith angle in Fig. 6. The probable errors are represented by the vertical lines. The curves drawn are both of the form

$$R_{(\beta)} = R_0 e^{-0.175\beta} \cos^2 \beta, \tag{12}$$

and the agreement with experimental values seems sufficiently good for us to use

$$f_{(\psi)} = f_{(\beta)} = e^{-0.175\beta} \cos^2 \beta = e^{-0.175\psi} \cos^2 \psi$$

for our intensity distribution function. This has been done in calculating the values in the last column of Table I.

The absorption of the counters and their shields was found to reduce the counting rate to $(87.1 \pm 1.7)\%$ of the incident value. This value omits the absorption of the thin wooden roof above the system and the top covering of the upper counter, since our experience, and that of Street and Woodward (21), shows that the number of detectable secondaries produced in this thin layer above the system very nearly cancels its absorption.

J_0 was calculated for each zenith angle, at the two altitudes, and mean values were found by weighting in proportion to the number of rays counted at each angle. These mean values were then corrected for efficiencies and absorption, and the final values are given in Table V. Also N_1 and N_2, calculated by means of Equations (9) and (10), are given in Table V.
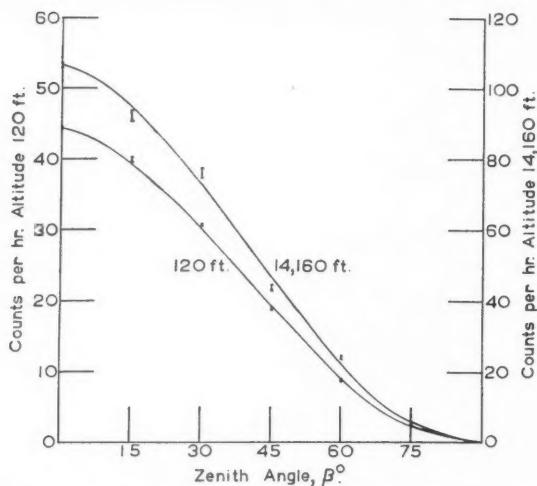
FIG. 6.   *The quadruple-coincidence counting rate as a function of zenith angle for altitudes of 120 and 14,160 ft.   The values are not corrected for absorptions or for efficiencies.*

Specific Ionization

Many observers have measured the ionization produced by cosmic rays. Millikan and Cameron (18), however, give absolute values taken at very nearly the same altitudes and latitudes as those of our stations, and we shall use their values for calculating the specific ionization.   From the table of values given by Millikan and Cameron, we find the number of ion pairs produced per cubic centimetre per second by cosmic rays in air at one atmosphere to be 2.48 and 10.31 at our lesser and greater altitudes respectively.   The specific ionizations, i, calculated from these values by means of Equation (11) are given in Table V.   The calculation of the probable errors quoted for the

TABLE V

Altitude, ft.	120	14,160
Mean specific ionization in ion pairs per centimetre in air at one atmosphere, i.	†54.8 ± 1.8 *82.0 ± 2.6	*87.5 ± 6
Total number of rays incident per hour per square centimetre of level surface, N_1.	78.3 ± 2.5	306 ± 22
Total number of rays incident per hour per square centimetre of surface normal to the rays, N_2.	109 ± 3.5	425 ± 30
Number of vertical rays incident per hour per square centimetre per unit solid angle, J_0.	58.4 ± 1.9	228 ± 15

† *Ionization chamber data from Clay and Jongen (4).*
* *Ionization chamber data from Millikan and Cameron (18).*

values of i involves an estimate of the probable errors in the results given by Millikan and Cameron. This estimate has been made from data given by them as an example of a typical run.

Discussion of Results

Measurements of the specific ionization produced by cosmic rays at sea level have been made by various observers using several different methods. Some of the results previously obtained are given below for comparison with the value obtained here, viz., 82.0 ± 2.6 ion pairs per cm. at sea level. Bothe and Kolhörster (3) found $i = 90$ per cm., and Messerschmidt (16), 110 per cm. Kolhörster and Tuwim (12) found $i = 135 \pm 13$ per cm. by taking counting rates with a single counter held with its axis at various orientations. Swann (22) found $i = 60$ per cm. by a direct ionization measurement with a linear amplifier. Evans and Neher (6) set an upper limit of 70 ± 10 per cm. from fluctuation measurements in an ionization chamber. Anderson (1) gives a value of 31 per cm., Locher (14) 36 per cm., and Kunze (13) 19 per cm., found by counting droplets along tracks in cloud chambers. It is obvious that the last method must lead to a lower limit. Anderson (1) estimates 122 per cm. from considerations of the energy loss of cosmic ray particles in passing through matter. Street and Woodward (21) give a value of 100 ± 3.7 per cm., and Kolhörster and Jánossy (11), 106 per cm., found by essentially the same method as that described here. Regener and Pfotzer (19) give $i = 103$ per cm. between altitudes 18 and 20 km. Danforth and Ramsey (5) obtain a value of 21 per cm. from considerations involving the efficiency of a single counter, but it seems that this must be a lower limit since they neglect wall effects. The arithmetic mean of all these values is in good agreement with our result.

Clay and Jongen (4) have recently given a value of 1.66 ions per cc. per sec. formed by cosmic rays at sea level in air at one atmosphere. This result has been corrected to a free air basis by taking the effects of the walls of the ionization chamber into account. Using this value we obtain for the specific ionization at sea level 54.8 ± 1.8 ion pairs per cm. which agrees well with values found by other methods. It is possible that all previous estimates of i, determined by the method described here, are too high because of the high value of the total ionization used.

The method used here for integration over the counter system gives a value differing by less than 1% from the value obtained by applying the equation given by Street and Woodward (21) to the system for $\beta = 0°$. The value quoted here for J_0, 58.4 ± 1.9 per sq. cm. per hr. per unit solid angle, at sea level is somewhat higher than that of Street and Woodward, viz., 48.0 ± 1.7 per sq. cm. per hr. per unit solid angle. The zenith angle distributions found for both altitudes were the same within experimental error. This result is in agreement with the work of Regener and Pfotzer (19). The distribution is definitely broader than that found by Johnson (7) at an altitude of 620 ft., but it is in good quantitative agreement with his result for an altitude of

6,280 ft.   In Peru, Johnson (8) finds the distribution to be slightly broader at sea level than at 14,200 ft.

The ratio of the total number of rays effective in ionization, N_2, at the higher station to that at the lower is 3.9 ± 0.3, and the ratio of the specific ionizations is 1.07 ± 0.08.   Johnson (8) finds 3.78 and 1.20 for these ratios for altitudes nearly the same in Peru.   Although the differences are not significant, the values found in Peru might be expected to be smaller than the others, since Johnson and Read (9) have shown that for a given altitude a lesser fraction of the shower-producing radiation than of the total is excluded, near the equator, by the earth's magnetic field.   The fact that the frequency of showers increases more rapidly with altitude than does the total radiation, causes the intensity, as determined by ionization chambers, to increase more rapidly than the coincidence counting rates, since only one count is registered for any number of particles passing through the counters simultaneously.   The ratio of specific ionizations given by Johnson (7) as 1.3 for altitudes of 6,280 and 620 ft. seems very high.   However, there is either a numerical or typographical error in this result*.   A correction reduces this value to about 1.2. This value would be still further reduced if it is found, as is expected from our work and Johnson's work in Peru, that the angular distribution is not broader at 6,280 ft. than at sea level.

References

 1. ANDERSON, C. D.   Phys. Rev. 44 : 406-416.   1933.
 2. BERNARDINI, G.   Nature, 129 : 578-579.   1932.
 3. BOTHE, W. and KOLHÖRSTER, W.   Z. Physik, 56 : 751-777.   1929.
 4. CLAY, J. and JONGEN, H. F.   Physica, 4 : 245-255.   1937.
 5. DANFORTH, W. E. and RAMSEY, W. E.   Phys. Rev. 49 : 854.   1936.
 6. EVANS, R. D. and NEHER, H. V.   Phys. Rev. 45 : 144.   1934.
 7. JOHNSON, T. H.   Phys. Rev. 43 : 307-310.   1933.
 8. JOHNSON, T. H.   Phys. Rev. 45 : 569-585.   1934.
 9. JOHNSON, T. H. and READ, D. N.   Phys. Rev. 51 : 557-564.   1937.
10. JOHNSON, T. H. and STREET, J. C.   J. Franklin Inst. 215 : 239-246.   1933.
11. KOLHÖRSTER, W. and JÁNOSSY, L.   Z. Physik, 93 : 111-122.   1934.
12. KOLHÖRSTER, W. and TUWIM, L.   Z. Physik, 81 : 435-439.   1933.
13. KUNZE, P.   Z. Physik, 83 : 1-18.   1933.
14. LOCHER, G. L.   Phys. Rev. 39 : 883-888.   1932.
15. MEDICUS, G.   Z. Physik, 74 : 350-378.   1932.
16. MESSERSCHMIDT, W.   Z. Physik, 78 : 668-688.   1932.
17. MILLIKAN, R. A.   Phys. Rev. 39 : 397-402.   1932.
18. MILLIKAN, R. A. and CAMERON, G. H.   Phys. Rev. 37 : 235-252.   1931.
19. REGENER, E. and PFOTZER, G.   Physik. Z. 35 : 779-784.   1934.
20. SKOBELZYN, D.   Compt. rend. 194 : 118-121.   1932.
21. STREET, J. C. and WOODWARD, R. H.   Phys. Rev. 46 : 1029-1034.   1934.
22. SWANN, W. F. G.   Phys. Rev. 44 : 961-968.   1933.
23. TUWIM, L.   Berlin Berichte, 19: 91-106, 360-373.   1931.

 *   *The existence of this error has been confirmed by private communication with Dr. Johnson.*

A STUDY OF THE JOULE AND JOULE-THOMSON EFFECTS[1]

By A. L. CLARK[2] AND L. KATZ[3]

Abstract

This paper contains material not treated in a previous paper on the same subject. It deals particularly with the Joule and Joule-Thomson effects at low and at high pressures and also near the critical point. These effects have been calculated by various methods from available data. The value of the internal pressure (Joule effect) has been calculated (for the first time) for the two-phase, liquid-vapor state, and compared with values obtained from the equation of state. This internal pressure is nearly a linear function of the external pressure. The values of the internal pressure have also been calculated for low pressure where values have been in doubt. The behavior of the specific heat at constant volume as a function of the temperature has also been studied and related to the behavior of the internal pressure. The inversion of the Joule and Joule-Thomson effects is examined. The internal pressure evidently rises to a maximum as the pressure is increased at constant temperature, and probably falls off to zero and becomes negative. For helium the pressure for inversion is relatively low. The inversion curve for the Joule-Thomson effect has also been studied, and it is shown that even for carbon dioxide an inversion of the effect may be expected. When the values of the two effects are small we must have recourse to experimental methods because the calculations cannot be made with accuracy. When however these values are large, calculations yield results of good accuracy, probably better than may be obtained by experiment.

In an earlier paper (3) one of the authors discussed the general relations for the perfect gas and the functions that may be used to measure the departure of real gases from the ideal gas. These expansion functions were given and their interrelations deduced. In particular, the Joule and Joule-Thomson effects were studied, and some calculated values of the magnitudes of these effects were given. The Joule effect is the change in temperature experienced by a gas when it expands into a vacuum, or expands without doing external work. The Joule-Thomson or Joule-Kelvin effect is the change in temperature experienced by a gas when it expands through a porous plug, or medium, or through a valve against an external pressure. The discussion of their values at low pressures and at temperatures below the critical temperature was reserved for a later paper. In the meantime new measurements and calculations have appeared, and there have been contributions to the general subject by several observers. During the past few months the work has been taken up anew, and the present paper gives the results of the investigation of points not discussed in the earlier paper.

As in the earlier paper

$$\lambda = \left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P \qquad (1)$$

has been taken as the measure of the Joule effect, and

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{W^*} = \frac{T\left(\frac{\partial v}{\partial T}\right)_P - v}{c_P} \qquad (2)$$

as the measure of the Joule-Thomson effect.   Roebuck (20) has taken

$$\eta = \left(\frac{\partial T}{\partial P}\right)_U, \qquad (3)$$

which he calls the Joule coefficient, to measure the Joule effect.   This is related to λ through the equation

$$\lambda = \left\{c_P\left(\frac{\partial P}{\partial v}\right)_T - P\left(\frac{\partial P}{\partial T}\right)_v\right\}\eta. \qquad (4)$$

λ as defined by Equation (1) may be interpreted either as the amount of energy required to maintain the temperature constant when unit mass of the gas expands by unit volume without doing external work, or as the internal or cohesion pressure. η is the ratio of the change of temperature to the change of pressure in the same expansion when there is no change in the internal energy. μ is the Joule-Thomson coefficient, or the ratio of the change in temperature to the change in pressure when the gas expands through the porous plug, or in any manner so as to emerge after expansion with negligible kinetic energy of flow.   The only external work is that done against the pressure existing on the exit side of the plug or orifice.   In other words the enthalpy remains constant.

The early experiments of Gay-Lussac, of Joule, and of Hirn, showed that λ is very small, so small that they were unable to detect its existence.   Indeed it is so small that it still is almost impossible to measure this quantity experimentally with any degree of accuracy.   In a paper by Keyes and Sears (10) some measurements of the Joule effect for carbon dioxide are given.   The temperature changes were of the order to be expected.   Roebuck (15), in a paper on the Joule-Thomson effect in air, has mentioned some unpublished work on the measurement of λ by one of his students.   The results again are of the proper order.

The senior author of the present paper has worked intermittently for some years with an apparatus for the direct measurement of both λ and η.   The experimental set-up is much like that used by Joule nearly 100 years ago. Compressed gas is allowed to expand suddenly into an evacuated chamber. The entire apparatus (tanks and valve) is immersed in a constant temperature bath.   A differential manometer is arranged so as to measure the change in pressure throughout the system immediately after expansion and later when the temperature has returned to that of the bath.   Values of λ and η are determined from measurements easily made, even with hydrogen.   None of the results have been published.

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* *W is the enthalpy $(U + Pv)$ per unit mass.*

The values for the internal pressure, λ, for carbon dioxide near the critical temperature and for nitrogen at temperatures between 0° and 150° C., have been calculated recently by Michels (11, 12, 13) and co-workers from their own $Pv - P$ data. The method of calculation will appear later in this paper. Roebuck has calculated both λ and η for a number of gases from his experimental values of μ. He has shown that η for helium is independent of the pressure but is positive at low temperatures (cooling), zero at $-70°$ C., and negative (heating) at high temperatures. To explain this unexpected result he takes into account the change in the number of collisions per unit time, per molecule, due to change in volume. Expansion brings about a change in the energy distribution. If the forces between the molecules are attractive, the speeding up of those taking part in the collisions represents an increase of kinetic energy. If the volume is increased, the number of collisions is decreased and the mean kinetic energy is lowered. Jeans (8, p. 190) is of the opinion that the amount of work obtainable from the change in the number of collisions on expansion is nil.

An excellent summary of the earlier work on the experimental determination of the Joule-Thomson coefficient will be found in a paper by Hoxton (7). For more recent data the bibliographies found in Roebuck's papers (15–20) should be consulted. μ for steam, and a bibliography of works on this substance, will be found in Report IV of the Steam Research Program, by F. G. Keyes, L. B. Smith, and H. T. Gerry. The most outstanding and painstaking work on the experimental determination of μ in recent years is that carried out by Roebuck and by Roebuck and Osterberg, using porous plugs of the radial flow type. The gases investigated were: air, helium, argon, nitrogen, and their mixtures.

Internal Pressure—Joule Effect

The free expansion coefficient, λ, as defined in Equation (1), may be interpreted either as the change in internal energy when unit mass of the gas expands by unit volume at constant temperature, or as the internal pressure. To show that λ *is* the internal pressure we use the general relation

$$dQ = dU + P\,dv,$$

from which

$$\left(\frac{\partial Q}{\partial v}\right)_T = \left(\frac{\partial U}{\partial v}\right)_T + P = \lambda + P, \tag{5}$$

and also

$$dQ = c_v dT + l_v dv, \tag{6}$$

where l_v may be regarded as either the total amount of energy required per unit mass per unit change of volume, the so-called latent heat of expansion, or as a pressure, such that an amount of energy $l_v dv$ is required to change a unit mass of gas through the volume dv against the pressure l_v, which is called the total or thermal pressure. From Equation (6) we obtain

$$l_v = \left(\frac{\partial Q}{\partial v}\right)_T. \tag{7}$$

Hence

$$l_v = \lambda + P, \tag{8}$$

i.e., the total pressure is the sum of the internal and external pressures.

Method of Calculation

Values of λ may be calculated by the graphical method used by Amagat, as was done by the senior author (3). This involves plotting the $Pv - P$ isotherms on a large scale. Then since the isometrics on such a diagram are straight lines through the origin, the corresponding values of P and T at constant volume may be obtained by means of a straight edge or a stretched thread. The $P - T$ isometrics are then drawn, and the values of the slope $\left(\dfrac{\Delta P}{\Delta T}\right)_v$ may be found for any pair of values of P and T, and the value of λ may be calculated by means of Equation (1).

The following method is a modification of the foregoing. The $Pv - P$ data may be interpolated to obtain the values of P and T at constant volume, so that the slope $\left(\dfrac{\Delta P}{\Delta T}\right)_v$ may be calculated. The accuracy with which λ can be determined by either method varies considerably over the range of available data, since it depends on the numerical difference between the values of $T\left(\dfrac{\Delta P}{\Delta T}\right)_v$ and P. When λ is large (high pressures and low temperatures) the accuracy is about the same as for P and T. When λ is small, however, the accuracy is determined by the position of the first significant figure in the difference. For example, if $T\left(\dfrac{\Delta P}{\Delta T}\right)_v - P = 13.247 - 13.157 = 0.090$, and if P and T are known to one part in 10,000, λ will be correct to about 5%.

The calculation may also be carried out as follows. Suppose the isometrics in terms of P and T have been drawn or the values tabulated. Then at any point P, T, where λ is to be calculated, a second point $P + \Delta P$, $T + \Delta T$ is taken. It is easily seen that

$$\lambda = T\left(\frac{P_{T+\Delta T} - P_T}{\Delta T}\right) - P_T = (T + \Delta T)\left(\frac{P_{T+\Delta T} - P_T}{\Delta T}\right) - P_{T+\Delta T}, \tag{9}$$

which gives the value of λ at a point approximately at the middle of the interval between the two points, or at $T + \dfrac{\Delta T}{2}$, $P + \dfrac{\Delta P}{2}$.

Again the average values of the derivatives on both sides of the point P, T may be taken so that

$$\lambda = T\frac{1}{2}\left(\frac{P_T - P_{T-(\Delta T)_1}}{(\Delta T)_1} + \frac{P_{T+(\Delta T)_2} - P_T}{(\Delta T)_2}\right) - P_T, \tag{10}$$

which is in some respects preferable. If $(\Delta T)_1 = (\Delta T)_2$, this reduces to Equation (9). Michels used Equation (9) for his calculations, while for

most of the work of this paper Equation (10) was used.   Table I shows the method and accuracy of a sample calculation, using Michel's (12) data for carbon dioxide, where the density of the gas was 28.1756 times the normal density.

TABLE I

SAMPLE CALCULATION OF λ BY MEANS OF EQUATION (10)

T, °C.	P, atm.	$\left(\dfrac{\Delta P}{\Delta T}\right)_v$	$\left(\dfrac{\Delta P}{\Delta T}\right)_v$, average	λ, atm.	Estimated accuracy, %
25.053	26.3707				
49.712	29.3972	0.12318	0.12165	9.879	0·1
75.260	32.4664	0.12013			

Saturated Two-phase Region

Within the saturated two-phase region

$$l_v = \frac{L}{v_1 - v_2},$$ (11)

where L is the ordinary latent heat per unit mass, v_1 is the specific volume of the higher phase (vapor), and v_2 that of the lower phase (liquid).   Then by Equation (8)

$$\lambda = \frac{L}{v_1 - v_2} - P.$$ (12)

Since for pure fluids P is the same for all volumes at the same temperature, L, v_1, and v_2 are constant, so that λ is a constant; *i.e.*,

$$(\lambda)_T = \text{constant}$$ (13)

or

$$(\lambda)_P = \text{constant},$$ (14)

where Equations (13) and (14) refer to the saturated two-phase region only.

Equation (12) may be deduced easily from the Clapeyron-Clausius equation, *viz.:*

$$\frac{\partial P}{\partial T} = \frac{L}{T(v_1 - v_2)}$$ (15)

$$\lambda = T\left(\frac{\partial P}{\partial T}\right)_v - P = \frac{L}{v_1 - v_2} - P.$$ (16)

It will be seen that λ, like P, is independent of the volume.   It remains constant from 100% liquid to 100% vapor, a fact that should be remembered when any theory of liquefaction is considered.   If λ is interpreted as an energy function, then during the process of vaporization at constant temperature, the internal energy is a linear function of the volume.   If, on the

other hand, λ is regarded as a pressure, the molecules are able to move apart during the process of evaporation without any change in the internal pressure. Further, from Equation (12) we obtain

$$L = (\lambda + P)(v_1 - v_2) = l_v(v_1 - v_2).\qquad(17)$$

$P(v_1 - v_2)$ is the external heat of vaporization, or the energy used in separating the molecules against the external pressure, while $\lambda(v_1 - v_2)$ is the internal heat of vaporization, or the energy used in separating the molecules against the internal pressure. The total heat of vaporization, L, is stored as potential energy, and is equal to the work done against the total pressure, l_v.

The reduced value of λ may be defined as

$$\Lambda = \theta\left(\frac{\partial \pi}{\partial \theta}\right)_\varphi - \pi,\qquad(18)$$

where θ, π, and φ are the reduced values of temperature, pressure, and volume defined as in van der Waals' original use of derived magnitudes, $i.e.$, the reduced temperature, pressure, and volume are the ratios of the actual temperature, pressure, and volume to the critical values of these quantities. It follows that

$$\Lambda = \frac{\lambda}{P_e}.\qquad(19)$$
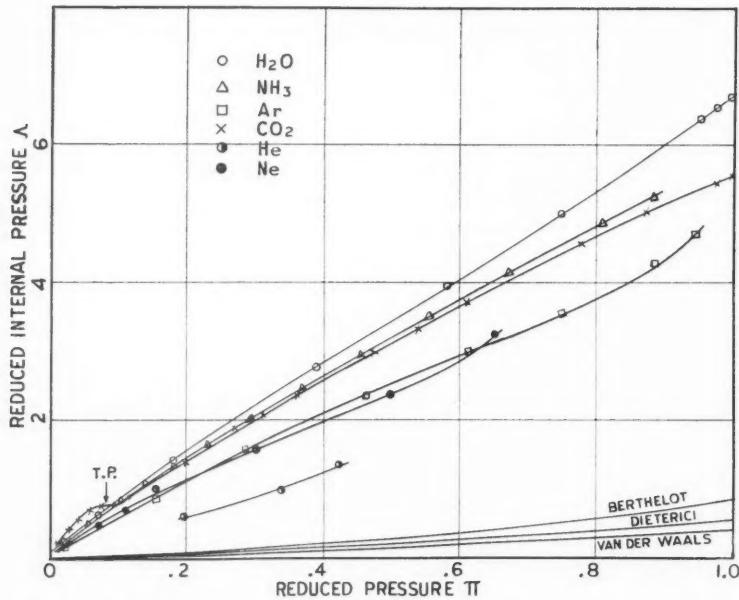
FIG. 1. *Internal pressure—saturated two-phase region. Water vapor pressure data of Keyes, Smith, and Gerry. All other data from Tables Annuelles Int. de Constants, Vol. 9, 1929. (T.P. = triple point of carbon dioxide).*

The reduced values for different gases may be calculated if the values of λ are determined by means of Equation (16), using saturated vapor pressure data. These values are shown in Fig. 1 plotted as a function of the reduced pressure. It will be seen that the internal pressure is nearly a linear function of the external pressure, the lines being slightly curved near each end. It follows that the internal pressure and the saturated vapor pressure expressed as functions of the temperature must be of nearly the same form.

Fig. 2 shows the values of λ along the critical isothermal plotted against the pressure, the results calculated by Michels (11) for carbon dioxide being used. Values of λ calculated from the saturated vapor data are also shown. The two curves intersect at the critical pressure. The curve calculated from the saturated vapor data is really the locus of the saturated vapor pressure points on a series of curves like that of Michels for various temperatures below the critical.
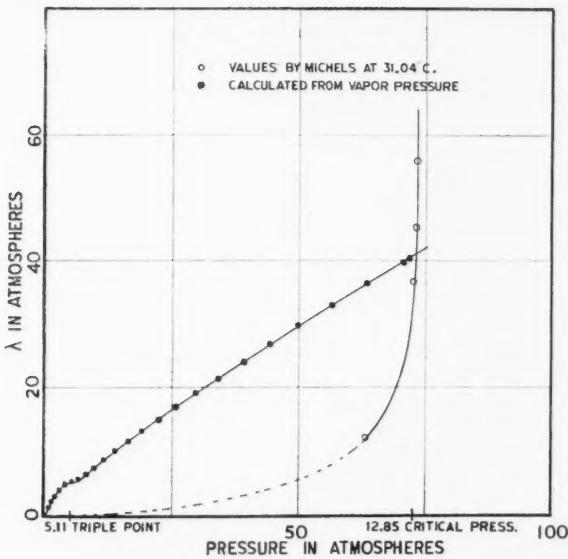
FIG. 2. *Internal pressure of carbon dioxide in the saturated two-phase region.*

Low Pressure Region—Equations of State

Since the first attempt by Hirn to correct the ideal gas equation, many equations of state have been proposed, each attempting to take into account the intermolecular forces and the actual total volume of molecules in order to obtain better agreement with the behavior of real gases. It seems evident that if such equations are to be applicable to the problems under discussion, they must yield values of the internal pressure comparable with those values calculated from $Pv - P$ data or observed directly. Conversely, the degree

of accuracy with which a certain equation of state may predict the magnitude of the internal pressure may be taken as a measure of its value in the application to problems involving internal energy, departure from the law of Joule, or any quantities depending on the variation of λ.

From van der Waals' reduced equation of state

$$\left(\pi + \frac{3}{\varphi^2}\right)\left(3\varphi - 1\right) = 8\theta$$

the value of Λ is

$$\Lambda = \frac{3}{\varphi^2} \tag{20}$$

or if $\pi\varphi = \frac{8}{3}\theta$ approximately,

$$\Lambda = \frac{27}{64}\frac{\pi^2}{\theta^2} . \tag{21}$$

The equation of state proposed by Dieterici in its reduced form is

$$\pi = \frac{\theta e^{2\left(1 - \frac{1}{\varphi\theta}\right)}}{2\varphi - 1} ,$$

which yields

$$\Lambda = \frac{2\pi}{\theta\varphi} . \tag{22}$$

If $\pi\varphi = \frac{e^2}{2}\theta$ (approximately), then

$$\Lambda = \frac{4}{e^2}\frac{\pi^2}{\theta^2} . \tag{23}$$

And finally the reduced equation of Berthelot, the empirical relations between T_c, P_c, and v_c, and the modified constants, a, b, and R suggested by him, being used, is

$$\left(\pi + \frac{16}{3}\frac{1}{\theta\varphi^2}\right)\left(\varphi - \frac{1}{4}\right) = \frac{32}{9}\theta .$$

Hence

$$\Lambda = \frac{32}{3}\frac{1}{\theta\varphi^2} . \tag{24}$$

If the approximate relation $\pi\varphi = \frac{32}{9}\theta$ is assumed, then

$$\Lambda = \frac{27}{32}\frac{\pi^2}{\theta^3} . \tag{25}$$

Values of Λ calculated from the equations of van der Waals and Dieterici differ only by a constant factor of 1.28316, the equation of van der Waals giving the lower value. Theoretically both equations have the same validity (9, p. 174), being true for the first order of quantities only. Figs. 3 and 4 show the reduced internal pressure as calculated by means of the above three equations of state and actual values for various substances calculated from $Pv - P$ data.

A few points for ether, calculated from the data of Keyes and Felsing (9), the semi-empirical equation of state of Hildebrand (6) being used, are also shown. This equation is of particular interest because it was developed from a consideration of attractive and repulsive molecular forces varying inversely with some powers of the distance.

λ is given by

$$\lambda = \left(\frac{\partial U}{\partial v}\right)_T = \frac{ma}{v^{m+1}}\left\{ 1 - \left(\frac{v_0}{v}\right)^{n-m}\right\} , \qquad (26)$$

where v is the molal volume at any temperature and pressure, and v_0 is the molal volume at zero pressure and at absolute zero. If λ is zero, then $v_0 = v$, which enables one to calculate the value of v_0, a value that is independent of the values of m and n. Hildebrand used the data of Keyes and Felsing and arrived at the equation for ether

$$\lambda = \frac{3180 \times 10^4}{v^2}\left\{ 1 - \left(\frac{79}{v}\right)^8\right\} , \qquad (27)$$

where $a = 3180 \times 10^4$, $m = 1$, $v_0 = 79$, and n is chosen empirically equal to 9. It will be remembered that the equation of van der Waals gives $\lambda = \frac{a}{v^2}$.
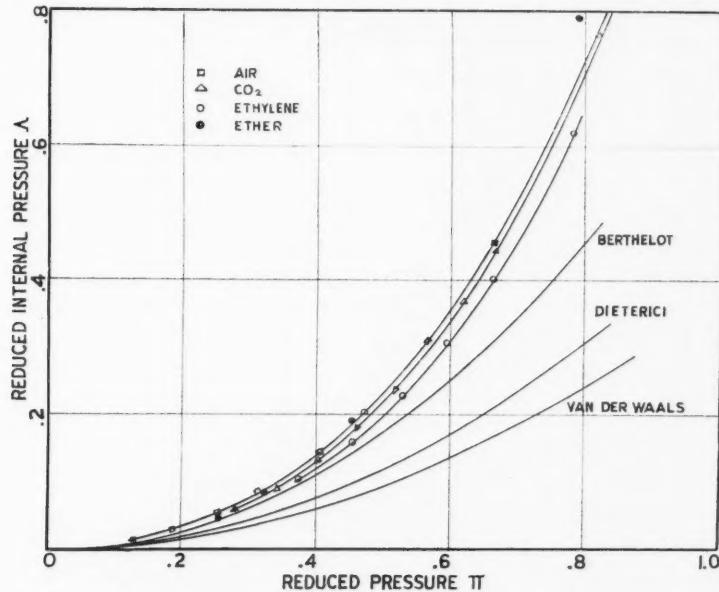
FIG. 3. *Reduced internal pressure at constant temperature* $\theta = 1 \cdot 061$. *Curves for air, carbon dioxide, and ethylene calculated by means of Equation (10). Curves for ether calculated by means of Equation (27). Data: Air—Witkowski, Penning and of Holborne and Otto. Carbon dioxide—A. Michels and C. Michels. Ethylene—A. Michels, J. de Gruyter, and F. Niessen. Ether—Keyes and Felsing.*
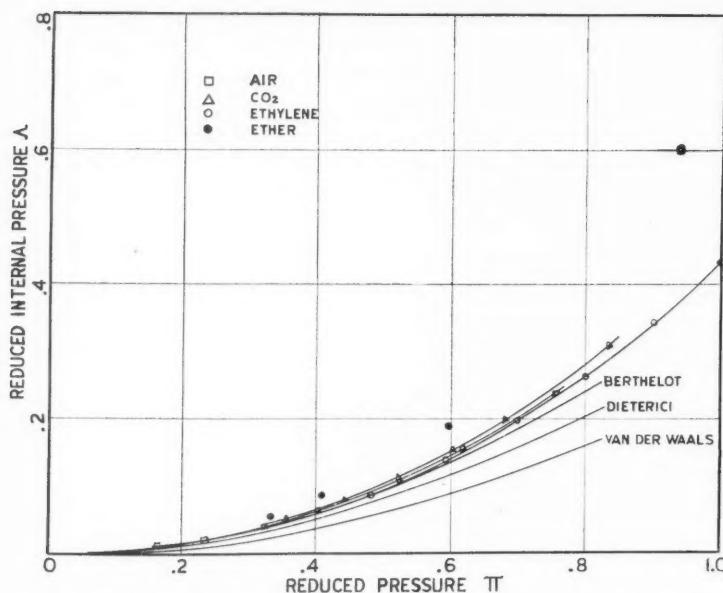
FIG. 4. *Reduced internal pressure at constant temperature θ = 1·309. Same as Fig. 3, only at a higher temperature.*

The graphs of Figs. 3 and 4 show that the equation of Berthelot gives results that are in fair agreement with the values calculated from P, v, T data even at pressures of $\pi = 0.5$, whereas the equations of van der Waals and of Dieterici give results that depart widely from these calculated results. As P approaches zero, $\left(\dfrac{\partial P}{\partial T}\right)_v$ also approaches zero, and therefore $\lambda = T\left(\dfrac{\partial P}{\partial T}\right)_v - P$ approaches zero. The agreement with the values calculated from P, v, T data shown by all three equations is better at low than at high pressures. Also the agreement at high temperatures is better than at low.

In general the equation of Berthelot shows best agreement with the calculated values. None of the equations however show λ increasing as rapidly with either temperature or pressure as is required by the graphs giving the calculated results.

In the two-phase, liquid-vapor region the values of λ obtained from the equations of state are low compared with those obtained from P, v, T data. Thus in Fig. 1, the three lower graphs were obtained by substituting the reduced value of P and the corresponding reduced values of T for water in Equations (21), (23), and (25). The resulting values of Λ were then plotted against π. These curves should be compared with the more accurate curve obtained by substituting the same saturated vapor data in Equation (16).

It is to be noted that the equations themselves do not yield unique internal pressure values for this region, but give the values of λ if the proper values of P and T (found experimentally) are used.

High Pressure

For all substances investigated, calculation shows that at low pressure the internal energy decreases upon isothermal compression, *i.e.*, $\left(\dfrac{\partial U}{\partial P}\right)_T$ is negative.   At a certain pressure, depending on the temperature, it reaches a minimum value and further compression causes it to increase.   Eventually $\left(\dfrac{\partial U}{\partial P}\right)_T$ becomes positive.

Now

$$\lambda = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial v}\right)_T . \tag{28}$$

Since $\left(\dfrac{\partial P}{\partial v}\right)_T$ is always negative*, λ is positive at low pressure, zero when $\left(\dfrac{\partial U}{\partial P}\right)_T = 0$, and negative at high pressure.   From Equations (8) and (11) the pressure at which λ is zero is given by

$$P = T\left(\frac{\partial P}{\partial T}\right)_v = l_v \tag{29}$$

(when the external pressure is the total pressure).

The pressure at which the internal energy is a minimum, $\left(\dfrac{\partial U}{\partial P}\right)_T = 0$ and $\lambda = 0$, varies greatly even with gases.   It varies from a few atmospheres with helium to thousands of atmospheres with other gases.†

Bridgman (2) finds that with liquids the pressure at which $\left(\dfrac{\partial U}{\partial P}\right)_T = 0$ is about 7000 atm. or higher.   For solids he gives values ranging from 5800 atm. for sodium at 30° C. to 21,000 atm. for iridium at the same temperature.

The curves of Figs. 5, 6, and 7 illustrate the general character of λ as a function of the external pressure at constant temperature.   The curves of Fig. 8 are plotted from values taken from Fig. 5 and show the variation of λ with temperature at constant pressure.   The agreement at 20 atm. with values given by Roebuck is seen to be very good.

* *The completely unstable region required by the equation of van der Waals is excluded.*

† *Bridgman (1) assigns a negative value to $\left(\dfrac{\partial U}{\partial P}\right)_T$ for helium at room temperatures up to pressures more than 15,000 atm., whereas Roebuck's calculations show λ to be negative even at atmospheric pressure and 0° C.   This would indicate that $\left(\dfrac{\partial U}{\partial P}\right)_T$ has already become positive at this low pressure.   The results obtained in this investigation, while not conclusive, show that λ is very small and certainly negative at even fairly low pressure.   This is in agreement with Roebuck's work.*
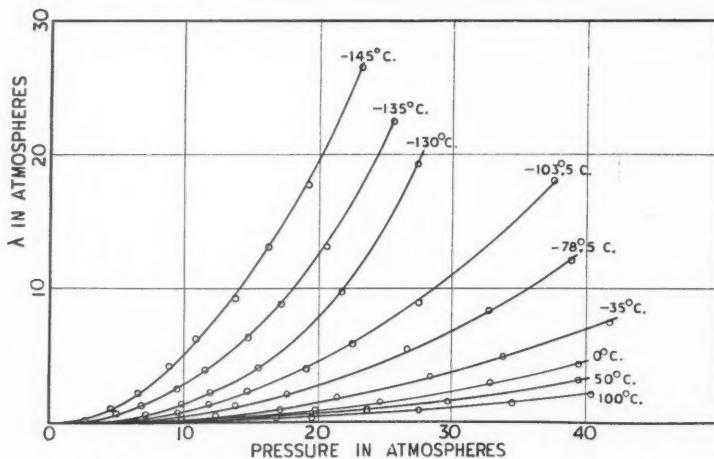
FIG. 5.   *Variation of* λ *with pressure at constant temperature.   Air.   Calculated by means of Equation (10) from Pv − P data of Witkowski, Penning, and of Holborne and Schultze.*
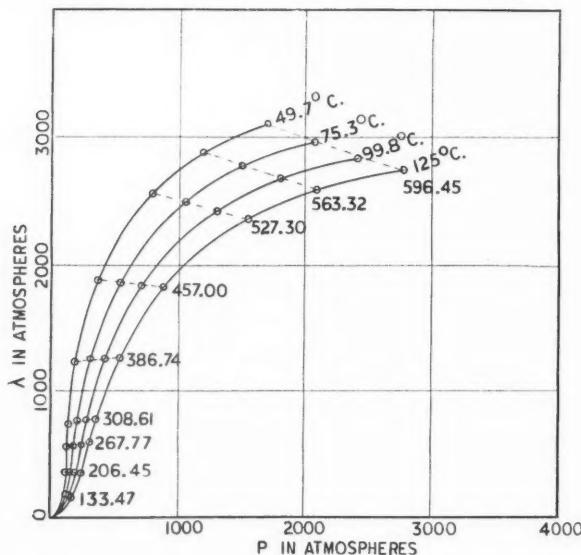

FIG. 6.   *Variation of* λ *with pressure at constant temperature. Carbon dioxide. Calculated by means of Equation (10) from Pv − P data of A. and C. Michels.   Points joined by dotted lines are at the same volume or density (numbers indicate density relative to that at N.T.P. as unit).*
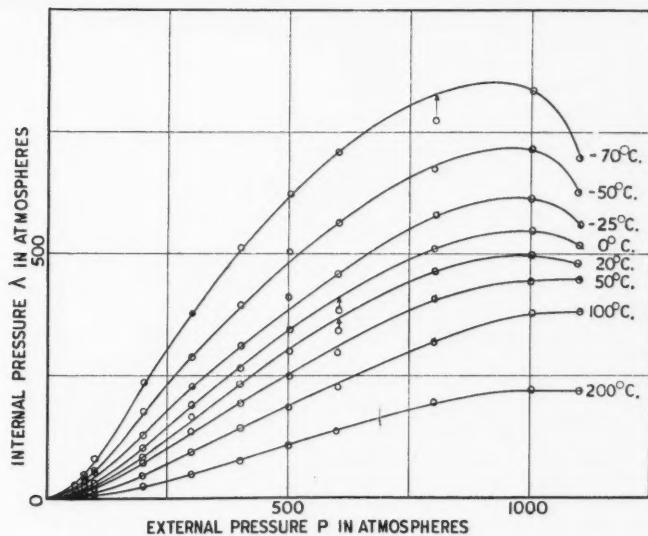
FIG. 7. *Variation of λ with pressure at constant temperature. Nitrogen.*

$$\lambda = T\left(\frac{\partial P}{\partial T}\right)_v - P = -\left\{\frac{\frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_P}{\frac{P}{v}\left(\frac{\partial v}{\partial P}\right)_T} + 1\right\}P$$

Values of $\frac{P}{v}\left(\frac{\partial v}{\partial P}\right)_T$, $\frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_P$, *and P are from data of W. E. Deming and L. E. Shupe.*

Note: *The values of λ calculated for 1200 atm. pressure are extremely erratic; no doubt extrapolated values given by Deming and Shupe are not sufficiently accurate.*

Specific Heat at Constant Volume

A study of the curves, Fig. 9, which show λ as a function of the temperature at constant volume, leads to interesting results. From Equation (1)

$$\left(\frac{\partial \lambda}{\partial T}\right)_v = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v = \left(\frac{\partial c_v}{\partial v}\right)_T. \qquad (30)$$

Since the slope of these curves is given by $\left(\frac{\partial \lambda}{\partial T}\right)_v = \left(\frac{\partial c_v}{\partial v}\right)_T$, it is seen that as one goes from curve to curve at constant temperature the slope becomes greater as the critical volume is approached, and the change in λ, and therefore c_v, is seen to become greater as the critical temperature is approached. Similarly, along any one of the curves (isometric) the slope increases as the critical temperature is approached, so c_v is an increasing function of the temperature.
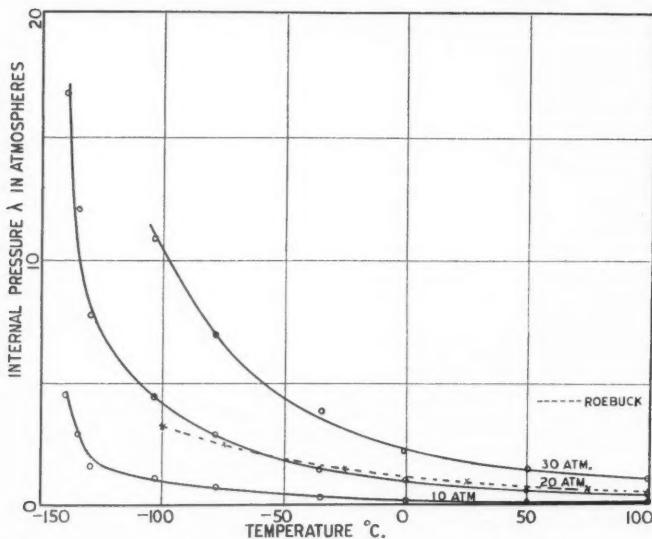
FIG. 8.   *Variation of* λ *with temperature at constant pressure. Air. Full lines were obtained by taking values off graphs in Fig. 5 at 10, 20, and 30 atm. pressure.   Dotted line shows values of* λ *calculated by Roebuck from his experimental values of* μ *for air at 20 atm. pressure.*

Young (21) has shown that $\left(\dfrac{\partial^2 P}{\partial T^2}\right)_v = 0$ for isopentane near the critical point.   This leads one to expect that the curves do not continue to rise indefinitely but pass through a maximum.   Recently Michels *et al.* (11) has calculated c_v for carbon dioxide, and has shown that it passes through a maximum near the critical point.   Where the value of c_v is a maximum, the following must hold—

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v = \left(\frac{\partial \lambda}{\partial T}\right)_v = 0 . \tag{31}$$

There is thus complete agreement between the behavior of c_v and that of λ studied as functions of the temperature at constant volume.

Joule-Thomson Effect

The Joule-Thomson coefficient defined by Equation (2) is the change in temperature per unit change of pressure experienced by a gas while expanding through a porous plug.   This effect is due to the departure of the gas from the laws of Boyle and Joule.   It may be shown that

$$\mu = -\frac{1}{c_P}\left(\frac{\partial W}{\partial P}\right)_T = -\frac{1}{c_P}\left(\frac{\partial (U + Pv)}{\partial P}\right)_T$$
$$= -\frac{1}{c_P}\left\{\lambda\left(\frac{\partial v}{\partial P}\right)_T + \left(\frac{\partial (Pv)}{\partial P}\right)_T\right\} . \tag{32}$$
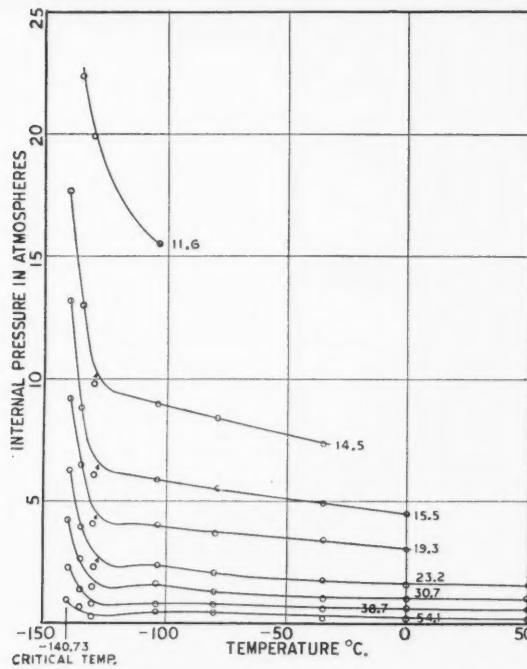
FIG. 9. *Variation of* λ *with temperatre at constant volume. Air. Calculated by means of Equation (10) from Pv−P data of Witkowski, Penning, and of Holborne and Schultze (see Fig. 5). Figures on graphs indicate the specific volume in cc. per gm., the critical specific volume being 2.86 cc. per gm. (not shown).*

If the gas obeyed the laws of Boyle and Joule, λ and $\left(\dfrac{\partial(Pv)}{\partial P}\right)_T$ would be zero, and so μ would be zero.

At low temperature and pressure, as has been noted, λ is generally positive (cooling on expansion), and since $\left(\dfrac{\partial v}{\partial P}\right)_T$ is always negative, the contribution of $\lambda\left(\dfrac{\partial v}{\partial P}\right)_T$ to μ is positive. Also, as Amagat has shown, $\left(\dfrac{\partial(Pv)}{\partial P}\right)_T$ is negative at sufficiently low temperature and pressure, and its contribution to μ is also positive. Thus μ, being the results of two effects, may be larger in magnitude than either and may be measurable when λ is not. If either the temperature or pressure is changed sufficiently, one or both effects may change sign, so that the value of μ may pass through zero and become negative, as experiment shows is true.

From the discussion in the first part of this paper, it is evident that λ is of greater theoretical importance than either μ or η, but because of the greater ease with which μ is measured and because of its application to the liquefaction of gases, it has received most attention.

Inversion Curve

Through an examination of the signs and magnitude of λ, $\left(\dfrac{\partial v}{\partial P}\right)_T$, and $\left(\dfrac{\partial (Pv)}{\partial P}\right)_T$, it may be shown that the points for which μ is zero trace out a curve on the $Pv - P$ diagram essentially as shown in Fig. 10. This is known as the inversion curve. Expansion of a gas between any two states represented by points within the area enclosed by the inversion curve results in cooling of the gas. Expansion between any two states represented by points on the diagram which are outside the curve will result in a heating of the gas. Finally, expansion across the curve will result in heating, cooling, or no effect, depending on the position of the initial and final states.
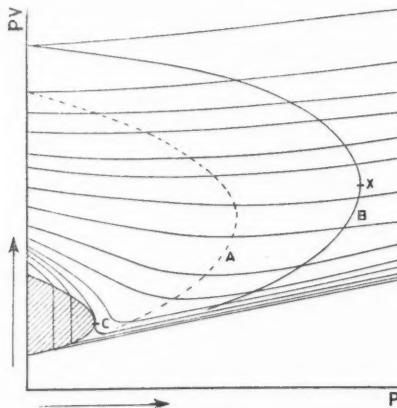
FIG. 10. *Inversion curve for μ. Dotted line, A, is the locus of points on the isothermals for which $\left(\dfrac{\partial (Pv)}{\partial P}\right)_T = 0$. Solid line, B, is the locus of points for which $\mu = 0$. Shaded area is the two-phase equilibrium region, and point C is the critical point. Expansion between any two pressures greater than X results in heating only.*

It is seen from the diagram that there is a pressure above which expansion between any two states (for all temperatures) results in heating only. This is to be expected, since, as the pressure increases, $\left(\dfrac{\partial (Pv)}{\partial P}\right)_T$ increases and is positive, whereas $\left(\dfrac{\partial v}{\partial P}\right)_T$ decreases rapidly. This explains why the first attempts of Kamerlingh Onnes to liquefy helium failed. The pressure before expansion was too high. Such a maximum pressure, and, as a matter of fact, the whole inversion curve, was predicted by Porter (14) from the equations of van der Waals and Dieterici, and has been confirmed experimentally by a number of investigators. Fig. 11 shows the inversion curve calculated from van der Waals' equation of state, with the reduced temperature and pressure as co-ordinates. On the same diagram the experimentally determined values of θ and π, for $\mu = 0$, for air and nitrogen given by Roebuck, and the calculated values for carbon dioxide from Fig. 12 are shown. Roebuck brought
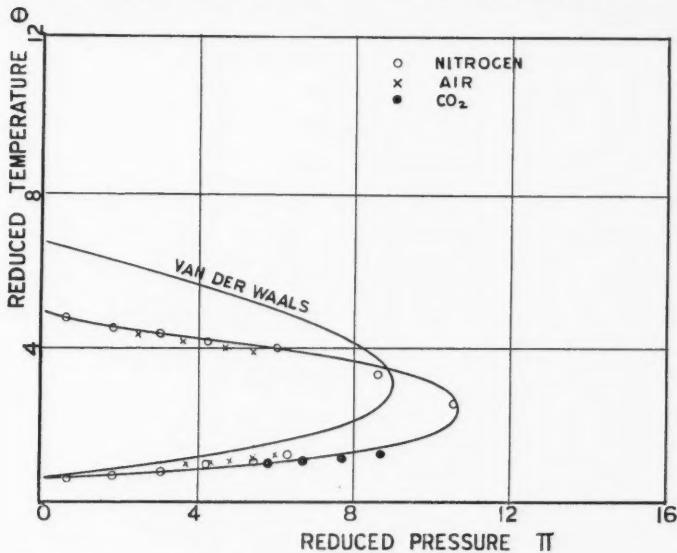
FIG. 11.   *Inversion curves for μ from van der Walls' equation and from experimental results. Nitrogen and air, from data by Roebuck; carbon dioxide, from our calculated curves, see Fig. 12.*

the upper and lower halves of the air inversion curve together at a maximum pressure somewhat lower than that given by van der Waals' equation.   If the law of corresponding states holds, the calculated maximum inversion pressure is greater than that given by van der Waals' equation as shown. It should also be noted that there is better agreement between the equation and experimental data in the low pressure, low temperature region.

Method of Calculation

Though μ has been measured experimentally by a number of investigators, the range is still very limited, and indirect methods of calculation have to be resorted to for extremely low or high temperatures.

One method is essentially the same as that described for λ, only in this case the isothermals on the $Pv - P$ diagram are cut by isopiestics to obtain values of Pv at T and $T + \Delta T$.

μ is calculated by means of the following relation:

$$\mu = \frac{1}{c_P P}\left\{ T\left(\frac{(Pv)_{T+\Delta T} - (Pv)_T}{\Delta T}\right) - (Pv)_T\right\}$$

$$= \frac{1}{c_P P}\left\{ (T + \Delta T)\left(\frac{(Pv)_{T+\Delta T} - (Pv)_T}{\Delta T}\right) - (Pv)_{T+\Delta T}\right\} , \qquad (33)$$

which gives μ at approximately the middle of the interval between the two points.
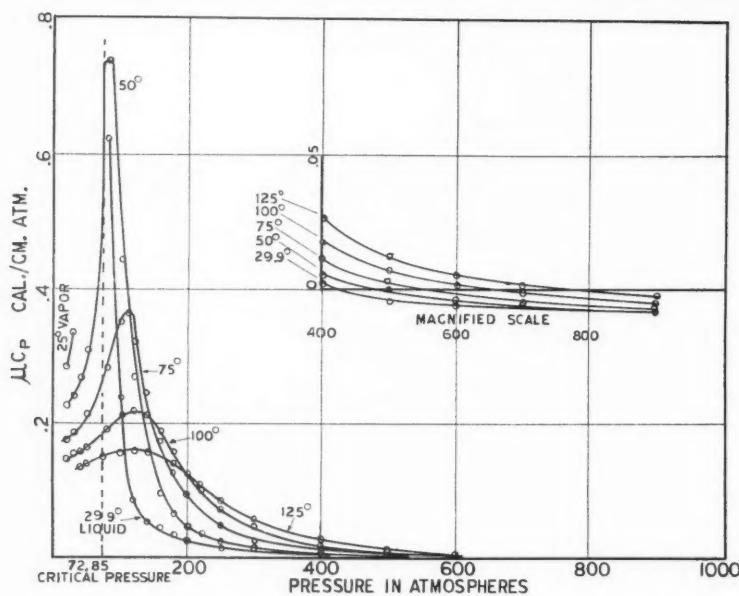
FIG. 12. μc_P for carbon dioxide.   Calculated by means of Equation (31) from $Pv - P$ data of Michels.

Deming and Shupe (4) used graphs of the residual quantity α to determine the derivative $\left(\dfrac{\partial \alpha}{\partial T}\right)_P$, and calculated μ from the equation:

$$\mu = \frac{T\left(\dfrac{\partial v}{\partial T}\right)_P - v}{c_P} = \frac{\alpha - T\left(\dfrac{\partial \alpha}{\partial T}\right)_P}{c_P} , \qquad (34)$$

where α is defined by:

$$\alpha = \frac{RT}{P} - v . \qquad (35)$$

The residual quantity method is more accurate for temperatures removed from the critical, since, at such temperatures, the $Pv - P$ isothermals are nearly straight lines, whereas the $\alpha - T$ isopiestics are quite curved and the slope $\left(\dfrac{\partial \alpha}{\partial T}\right)_P$ is measured with greater precision.

More recently Edmister (5) employed the residual quantity method to calculate μ for methane; the derivative $\left(\dfrac{\partial \alpha}{\partial T}\right)_P$ was determined by the chord area method of graphical differentiation on a large-scale plot.

TABLE II

CRITICAL CONSTANTS USED

Substance	Critical pressure, atm.	Critical temperature, °K.	Substance	Critical pressure, atm.	Critical temperature, °K.
He	2.261	55.19	Ethylene	49.98	282.65
Ne	26.86	44.38	CO_2	72.85	304.19
Air	37.25	132.42	NH_3	111.50	405.55
Ar	47.996	150.65	H_2O	217.88	647.85
Ether	36.7	467.7			

References

1. BRIDGMAN, P. W.   Modern Physics, 7 : 1-33.   1935.

2. BRIDGMAN, P. W.   The physics of high pressure.   G. Bell and Sons, Ltd., London.   1931.

3. CLARK, A. L.   Trans. Roy. Soc. Can. 18, III : 293-311.   1924.

4. DEMING, W. E. and SHUPE, L. E.   Phys. Rev. 37 : 638-654.   1931.

5. EDMISTER, W. C.   Ind. Eng. Chem. 28 : 1112-1116.   1936.

6. HILDEBRAND, J. H.   Phys. Rev. 34 : 984-993.   1929.

7. HOXTON, L. G.   Phys. Rev. 13 : 438-479.   1919.

8. JEANS, J. J.   The dynamical theory of gases.   Second edition.   Cambridge University Press, London.   1916.

9. KEYES, F. G. and FELSING, W. A.   J. Am. Chem. Soc. 41 : 589-619.   1919.

10. KEYES, F. G. and SEARS, F. W.   Proc. Natl. Acad. Sci. U.S. 11 : 38-41.   1925.

11. MICHELS, A., BIJL, A., and MICHELS, C.   Proc. Roy. Soc. London, A, 160 : 376-384. 1937.

12. MICHELS, A. and MICHELS, C.   Proc. Roy. Soc. London, A, 153 : 201-214.   1935.

13. MICHELS, A., WOUTERS, H., and DE BOER.   Physica, 1 : 587-594.   1934.

14. PORTER, A. W.   Phil. Mag. 111 : 554-568.   1906.

15. ROEBUCK, J. R.   Proc. Natl. Acad. Arts Sci. 60 : 537-596.   1925.

16. ROEBUCK, J. R.   Proc. Natl. Acad. Arts Sci. 64 : 287-334.   1930.

17. ROEBUCK, J. R. and OSTERBERG, H.   Phys. Rev. 43 : 60-69.   1933.

18. ROEBUCK, J. R. and OSTERBERG, H.   Phys. Rev. 45 : 332-340.   1934.

19. ROEBUCK, J. R. and OSTERBERG, H.   Phys. Rev. 46 : 786-790.   1934.

20. ROEBUCK, J. R. and OSTERBERG, H.   Phys. Rev. 48 : 450-457.   1935.

21. YOUNG, S.   Proc. Phys. Soc. London, 13 : 602-657.   1895.
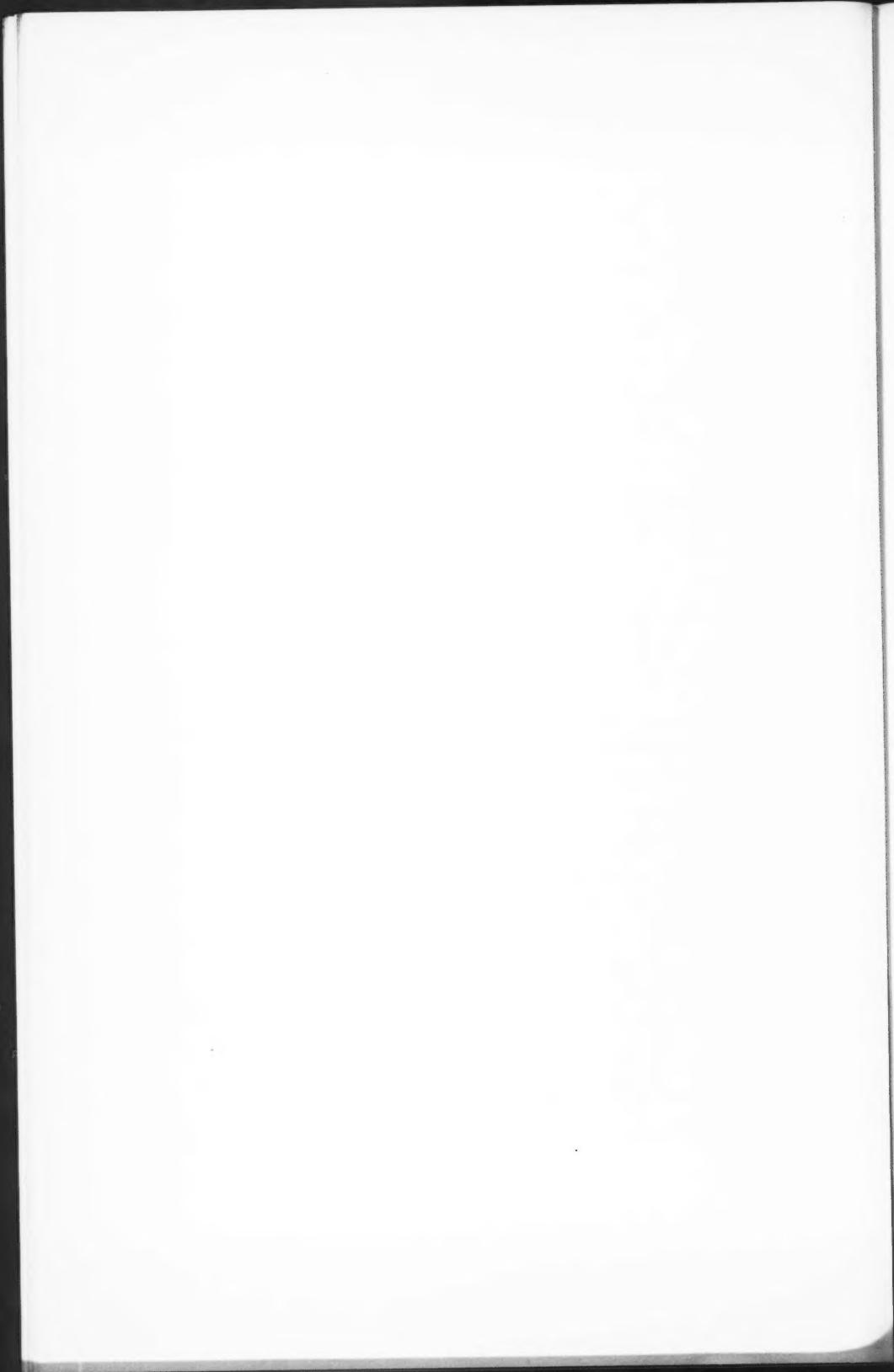
CONTRIBUTION TO THE STUDY OF THE PRECIPITATION OF CHROMATES[1]

By P. E. Pelletier[2], L. Cloutier[3], and Paul E. Gagnon[3]

Abstract

A study was made of the precipitation of the chromates of copper, cadmium, cobalt, zinc, and iron at room temperature. The concentration of the reacting metallic salt solutions was kept constant, and that of the potassium chromate solutions was varied regularly. Solutions were mixed in less than one-tenth of a second, and the rate of mixing was accurately determined. The ratio of oxide to chromium trioxide was found by analysis for chromium trioxide and the metal on the same portion of the precipitate. If the ratio remained constant with varying concentrations of reactants, a definite compound was indicated. The composition of the precipitates obtained with copper salts approached that of the normal chromate. Cadmium and cobaltous salts always gave normal chromates. Zinc and ferric salts yielded only basic mixtures.

Introduction

The products obtained in a great number of reactions often vary according to the mode of mixing the reagents. This is especially true with solutions which, upon mixture, are likely to give rise to basic compounds. Thus Thümmel (18) noticed that in pouring a solution of alkaline carbonate into a solution of mercuric chloride, mercuric oxychloride is formed, while if the solution of mercuric chloride is added to that of the alkaline carbonate, mercuric oxide is precipitated. Such solutions, according to the method in which the precipitation is carried out, usually give a series of mixtures the composition of which varies between that of the hydroxide and that of the less basic compound. These mixtures have sometimes been considered as definite compounds. This explains the great number of basic compounds mentioned in the literature.

Therefore, when it is possible to obtain a number of precipitates and it is desired to obtain one of constant composition, it is important that the reactants be mixed not only in given proportions but also as intimately as possible, in minimum time, before the precipitate is formed (8).

For this purpose Jolibois (9) designed an apparatus with which he systematically studied various precipitations (10).

One of the authors applied the same technique to the precipitation of lead chromates. He found that not only a normal chromate, but also two definite

basic compounds (2), were formed. In view of these results the authors decided to undertake the study of the precipitation of the chromates of copper, cadmium, cobalt, zinc, and iron.

The composition of the precipitates obtained with copper salts approached that of the normal chromate when the concentration of the potassium chromate solutions was increased regularly. The salts of cadmium and cobalt (cobaltous) gave only normal chromates. No definite compound was obtained with zinc or ferric salts.

The authors have also studied the action of mixtures of potassium hydroxide and potassium chromate on the above-mentioned salts. In every experiment they obtained only precipitates the basicity of which increased very rapidly to that of the hydroxide as the value of the ratio of potassium oxide to chromium trioxide in the solutions increased. Under similar conditions, the lead salts furnished two definite basic chromates (2).

Apparatus

The authors deem it desirable to repeat here the description of the apparatus and procedure (3) employed (Fig. 1).
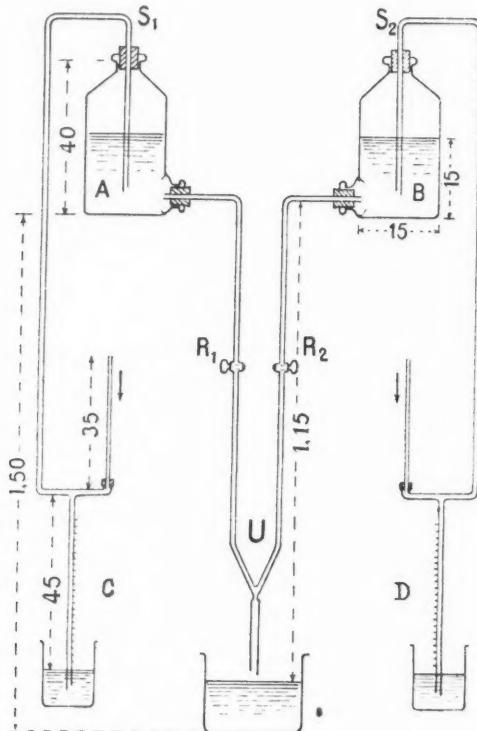

FIG. 1.   *Mixing apparatus.*

"The apparatus consists of two Mariotte flasks in which are placed two solutions A and B of known concentrations. By means of two stopcocks, R_1 and R_2, the flow of the solutions in the two tubes, which are joined in U, can be regulated. At the point U, the solutions mix very rapidly in less than 1/10th of a second. A precipitate is then formed in a homogeneous liquid. Air is drawn into the Mariotte flasks according to the rate of flow of the liquids. The rate of flow is measured by means of two Venturi tubes, *i.e.*, two capillary tubes and two coloured solutions.

"The apparatus is calibrated in such a way that when the coloured liquids are at the same level in the two tubes C and D, the rates of flow are the same."

"Such an apparatus enables us to study systematically a precipitation. We keep the concentration of the solution A constant, we precipitate with different solutions B of increasing concentration and each time we study the composition of the precipitate."

A curve can be constructed by plotting the different values of the molar ratio of oxide to chromium trioxide in the precipitates against the molar ratio of chromium trioxide to oxide in the solutions.

If the composition of the precipitates remains constant with varying concentrations of reagent B, in different experiments, only one phase is present, *i.e.*, one definite compound (12). A mixture is indicated if, under the same conditions, the composition of the precipitate varies.

Results

Copper Chromates

Vauquelin (19) stated that when potassium chromate is added to a solution of a neutral copper salt, a chestnut brown precipitate is formed, which, according to Gerhardt (6) and Freese (4), consists of $K_2O . 3CuO . 3CrO_3 . 2H_2O$, or according to Gröger (7), of $KCu_2(OH)(CrO_4)_2 . H_2O$. Skormin (17) obtained the compound $4CuO . CrO_3 . 3H_2O$ by the action of an alkaline solution of potassium chromate in excess on a solution of copper sulphate. According to Rosenfeld (15, 16), the compound $3CuO . CrO_3 . 2H_2O$ is formed when potassium chromate is added to a solution of copper sulphate.

None of the compounds mentioned were obtained by the present authors, who treated solutions of copper nitrate, $M/20$, with solutions of potassium chromate that ranged in concentration from $M/40$ to $5/8\ M$.

The composition of the precipitate obtained approximates that of the compound $K_2O . 3CuO . 3CrO_3 . 2H_2O$ analyzed by Gerhardt (6) and Freese (4). However, the former precipitate has a greater proportion of copper than the latter. Furthermore, by means of a test with perchloric acid on a portion of the solution containing the dissolved precipitates, the authors have proved the total absence of potassium in each of the precipitates obtained.

The precipitates were filtered off, washed with cold water until free from potassium chromate, and dried at 80° C.; 0.5 to 1.0 gm. of the precipitate was then heated with 10 cc. of 10% potassium hydroxide solution, and the whole diluted to 200 cc. Copper hydroxide was filtered off, and well washed with hot water—until it did not contain any chromium. It was then dissolved in 12% sulphuric acid and the copper was determined electrolytically.

The filtrate from the copper hydroxide contained potassium chromate which was determined by iodometric titration.

The results obtained are given in Table I and Fig. 2.

TABLE I

COPPER NITRATE ($M/20$) AND POTASSIUM CHROMATE ($M/40$ to $5/8$ M)

Conc. of solutions, moles per litre		Molar ratio CrO_3/CuO in solutions	Analysis of precipitates, gm.		Molar ratio CuO/CrO_3 in precipitates	Average
$Cu(NO_3)_2$	K_2CrO_4		CuO	CrO_3		
0.05	0.025	0.5	0.4380	0.2082	2.644	
			0.3091	0.1459	2.664	
			0.5405	0.2577	2.636	2.64
0.05	0.05	1.0	0.5784	0.2845	2.555	
			0.4400	0.2174	2.540	
			0.5154	0.2465	2.568	
			0.4549	0.2248	2.548	2.55
0.05	0.075	1.5	0.3755	0.2645	1.780	
			0.2999	0.2123	1.776	1.78
0.05	0.10	2.0	0.4857	0.4736	1.289	
			0.3169	0.3169	1.282	1.28
0.05	0.15	3.0	0.2009	0.2108	1.181	
			0.2736	0.2932	1.173	
			0.2740	0.2889	1.165	1.17
0.05	0.20	4.0	0.2596	0.2799	1.165	
			0.2594	0.2819	1.157	1.16
0.05	0.25	5.0	0.2985	0.3382	1.110	
			0.2694	0.3059	1.110	1.11
0.05	0.30	6.0	0.2506	0.2862	1.101	
			0.2581	0.2969	1.092	1.10
0.05	0.40	8.0	0.2364	0.2739	1.092	
			0.2021	0.2336	1.088	1.09
0.05	0.50	10.0	0.2924	0.3416	1.076	
			0.2556	0.2999	1.071	1.07
0.05	0.625	12.5	0.2737	0.3286	1.062	1.06

Cadmium Chromates

Several basic chromates of cadmium were prepared from boiling solutions of a cadmium salt and potassium chromate: $3CdO.2CdCrO_4.8H_2O$ (13); $CdO.CdCrO_4.H_2O$ (5); $4CdO.3CdCrO_4$ with 4.5 to 6.0 H_2O (17).

The nature of the product obtained depends on the time of contact of the precipitate with boiling water. Consequently, the composition of the basic salts of cadmium chromate remains to be determined.

A solution of cadmium nitrate, $M/20$, was used. The concentration of the potassium chromate solutions varied from $M/20$ to $M/2$. By precipitating at room temperature, only the normal chromate was obtained, whatever the concentration.
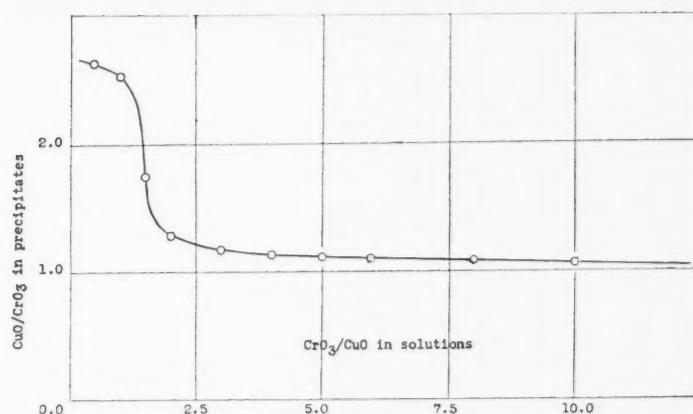
FIG. 2. *Copper nitrate and potassium chromate.*

The precipitates, dried at 80° C., were dissolved in dilute acetic acid, and chromium was determined by the usual method as lead chromate. The filtrate was then treated with sulphuric acid and the excess of lead was removed as lead sulphate. The cadmium was then precipitated with potassium carbonate and determined as cadmium oxide.

Table II and Fig. 3 show the results obtained.

TABLE II

CADMIUM NITRATE ($M/20$) AND POTASSIUM CHROMATE ($M/20$ to $M/2$)

Conc. of solutions, moles per litre		Molar ratio CrO_3/CdO in solutions	Analysis of precipitates, gm.		Molar ratio CdO/CrO_3 in precipitates	Average
$Cd(NO_3)_2$	K_2CrO_4		CdO	CrO_3		
0.05	0.05	1.0	0.3836	0.2977	1.004	
			0.3591	0.2784	1.005	1.00
0.05	0.10	2.0	0.4017	0.3111	1.006	
			0.3085	0.2389	1.006	1.01
0.05	0.25	5.0	0.5210	0.4084	0.998	
			0.4893	0.3773	1.001	1.00
0.05	0.50	10.0	0.3283	0.2583	0.990	
			0.4254	0.3291	1.007	1.00

Cobaltous Chromates

Briggs (1) prepared the normal cobaltous chromate by mixing solutions of cobaltous acetate and potassium chromate.

The authors likewise obtained a normal chromate by treating a solution of cobaltous nitrate, $M/20$, with different solutions of potassium chromate, $M/20$ to $M/2$. Under the conditions of the experiments, the basic compounds mentioned in the literature were not obtained.
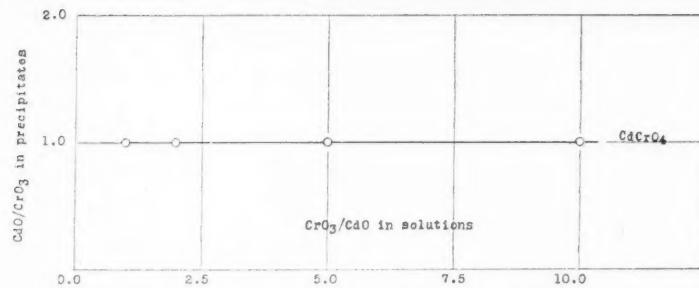
FIG. 3.   *Cadmium nitrate and potassium chromate.*

The precipitates, dried at 80° C., were treated with 20% potassium hydroxide, water was added, and cobalt hydroxide was filtered off.   After complete removal of potassium chromate by washing with hot water, chromium was determined in the filtrate by iodometric titration.   The cobalt hydroxide was dissolved in a mixture of hydrogen peroxide and dilute sulphuric acid, and the cobalt was determined electrolytically.

The results are shown in Table III and Fig. 4.

TABLE III

COBALT NITRATE ($M/20$) AND POTASSIUM CHROMATE ($M/20$ TO $M/2$)

Conc. of solutions, moles per litre		Molar ratio CrO_3/CoO in solutions	Analysis of precipitates, gm.		Molar ratio CoO/CrO_3 in precipitates	Average
$Co(NO_3)_2$	K_2CrO_4		CoO	CrO_3		
0.05	0.05	1.0	0.1457	0.1979	0.983	
			0.2317	0.3081	1.000	0.99
0.05	0.15	3.0	0.1565	0.2085	1.002	
			0.1561	0.2081	1.001	1.00
0.05	0.25	5.0	0.1376	0.1852	0.991	
			0.3455	0.4645	0.990	0.99
0.05	0.50	10.0	0.1837	0.2408	1.015	
			0.1474	0.1937	1.015	1.01

FIG. 4.   *Cobalt nitrate and potassium chromate.*

Zinc Chromates

The normal zinc chromate is difficult to prepare, owing to the fact that in the presence of a large amount of water it is readily hydrolyzed to basic salts. This is the reason why a great many basic salts have been reported. A number of these salts of indefinite composition form the so-called zinc yellow.

A solution of zinc nitrate, $M/20$, was treated with solutions of potassium chromate ranging in concentration from $M/20$ to $3/4\ M$.

The precipitates, dried at 80° C., were dissolved in dilute acetic acid. Chromium was determined as lead chromate. The excess of lead was removed as lead sulphate, and the zinc was then determined as zinc ammonium phosphate.

The results obtained are given in Table IV and Fig. 5.
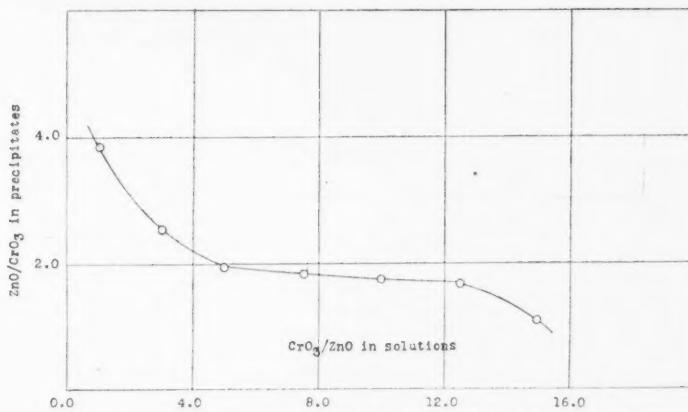
FIG. 5.   *Zinc nitrate and potassium chromate.*

TABLE IV
ZINC NITRATE ($M/20$) AND POTASSIUM CHROMATE ($M/20$ to $3/4\ M$)

Conc. of solutions, moles per litre		Molar ratio CrO_3/ZnO in solutions	Analysis of precipitates, gm.		Molar ratio ZnO/CrO_3 in precipitates	Average
$Zn(NO_3)_2$	K_2CrO_4		ZnO	CrO_3		
0.05	0.05	1.0	0.3325	0.1057	3.864	
			0.5268	0.1675	3.864	3.86
0.05	0.15	3.0	0.2769	0.1353	2.514	
			0.3741	0.1820	2.526	2.52
0.05	0.25	5.0	0.4255	0.2773	1.886	
			0.2730	0.2218	1.882	1.88
0.05	0.375	7.5	0.3214	0.2197	1.798	
			0.3510	0.2396	1.781	1.78
0.05	0.50	10.0	0.4836	0.3381	1.769	
			0.2452	0.1723	1.759	
			0.2380	0.1652	1.770	1.77
0.05	0.625	12.5	0.2453	0.1764	1.710	
			0.2872	0.2078	1.699	1.70
0.05	0.75	15.0	0.3788	0.3782	1.179	
			0.3073	0.3185	1.186	
			0.1826	0.1908	1.177	
			0.1889	0.1965	1.182	1.18

Iron Chromates

A solution of ferric chloride, $M/10$, was treated with solutions of potassium chromate of concentrations from $M/10$ to $M/2$.

The precipitates, dried at 80° C., were dissolved in dilute hydrochloric acid (10%). Iron was determined as ferric oxide, and chromium as sesquioxide or volumetrically by iodometric titration.

No definite compound was obtained, as is shown in Table V and Fig. 6.
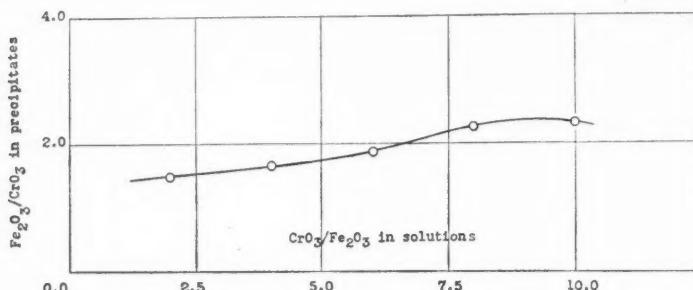
FIG. 6.   *Ferric chloride and potassium chromate.*

TABLE V

FERRIC CHLORIDE ($M/10$) AND POTASSIUM CHROMATE ($M/10$ to $M/2$)

Conc. of solutions, moles per litre		Molar ratio CrO_3/Fe_2O_3 in solutions	Analysis of precipitates, gm.		Molar ratio Fe_2O_3/CrO_3 in precipitates	Average
$FeCl_3$	K_2CrO_4		Fe_2O_3	CrO_3		
0.10	0.10	2.0	0.2383	0.0992	1.503	
			0.2168	0.0910	1.492	
			0.2118	0.0871	1.523	1.51
0.10	0.20	4.0	0.2305	0.0824	1.665	
			0.2288	0.0847	1.643	
			0.2701	0.1020	1.660	1.65
0.10	0.30	6.0	0.3323	0.1105	1.883	
			0.1937	0.0648	1.871	1.88
0.10	0.40	8.0	0.3360	0.0930	2.262	
			0.1901	0.0525	2.268	2.26
0.10	0.50	10.0	0.3441	0.0922	2.327	
			0.2281	0.0613	2.330	
			0.1887	0.0508	2.327	2.33

References

1. BRIGGS, S. H. C.   Z. anorg. chem. 63 : 325-329.   1909.
2. CLOUTIER, L.   Ann. chim. (10) 19 : 2-77.   1933.
3. CLOUTIER, L., PELLETIER, P. E., and GAGNON, P. E.   Trans. Roy. Soc. Can. III, 30 : 149-164.   1936.

4. FREESE, C.   Ann. Physik, 140 : 242-253.   1870.

5. FREESE, C.   Ber. 2 : 476-479.   1868.

6. GERHARDT, C.   J. Pharm. Chim. (3) 22 : 57.   1847.

7. GRÖGER, M.   Sitzber. Akad. Wiss. Wien, 113 : 155-171.   1903.

8. JOLIBOIS, P.   Bull. soc. chim. ind. (5) I : 597-613.   1934.

9. JOLIBOIS, P.   Compt. rend. 169 : 1095-1098.   1919.

10. JOLIBOIS, P., BOSSUET, R., and CHEVRY.   Compt. rend. 172 : 373-375.   1921.

11. JOLIBOIS, P. and BOSSUET, R.   Compt. rend. 174 : 1625-1628.   1922.

12. JOLIBOIS, P. and CLOUTIER, L.   Compt. rend. 195 : 795-797.   1932.

13. MALAGUTI, F. J. and SARZEAU, M.   Ann. chim. phys. (3) 9 : 431-463.   1844.

14. MILLER, W. H. and KENRICK, F. B.   J. Phys. Chem. 7 : 259-268.   1903.

15. ROSENFELD, M.   Ber. 12 : 954-959.   1879.

16. ROSENFELD, M.   Ber. 13 : 1469-1475.   1880.

17. SKORMIN, B.   Dissert.   Berlin.   1896.

18. THÜMMEL, K.   Arch. Pharm. 223 : 953-973.   1885.

19. VAUQUELIN, M.   Ann. chim. phys. (1) 70 : 70-94.   1809.

WILDIERS' BIOS AND THE LACTIC ACID BACTERIA[1]

THE RELATION OF BIOS TO THE WATER-SOLUBLE B-VITAMINS

By Blythe Alfred Eagles[2], Olga Okulitch[3], and
Arthur Stephen Kadzielawa[4]

Abstract

The influence of three distinct activators prepared from tomatoes, yeast, or liver, on the metabolism of two species of lactic acid bacteria has been studied. One of these activators is Bios II *A*, and the other two have been shown to be components constituting Bios II *B*. On the basis of their physical and chemical properties, it is suggested that the growth stimulants required by the lactic acid bacteria are identical with certain of the heat-stable accessory food factors of the Vitamin-B complex essential for the growth of animals.

In two papers (3, 16) from this laboratory it was shown that the Bios of Wildiers exerts a marked influence on the acid-producing abilities of the lactic acid bacteria. In addition, evidence in support of the multiple nature of Wildiers' Bios as demonstrated by Miller, Eastcott, and Maconachie (13) for the growth of yeasts, was presented for the betacocci and those streptococci which normally find milk a poor nutrient substrate. Enrichment of milk with three distinct activators (Bios I, Bios II *A*, and Bios II *B*) prepared from alfalfa, yeast, or tomatoes, evidently provided not only ideal growth conditions for these micro-organisms, but a substrate as well for their most intensive metabolism.

The vitamin requirements of the lactic acid bacteria have been investigated by Orla-Jensen and co-workers (14). They have demonstrated that all true lactic acid bacteria require two activators, lactoflavin and "milk bios". "Milk bios" is a thermostable, alkali-fast substance present in milk and adsorbed by activated charcoal. It is considered to be identical with pantothenic acid described by Williams and Saunders (20); and it is also suggested by Orla-Jensen and co-workers that it is identical with Vitamin B_6 (1, 8). Further, they have shown that the lactic acid rod forms require in addition to lactoflavin and "milk bios" an activator present in whey and not adsorbed by activated charcoal. Vitamin B_1 was found to play no role in the physiological activities of the lactic acid micro-organisms.

In a study of the accessory nutritive factors required by the lactic acid bacteria, Snell, Strong, and Peterson (17) have recently reported the presence, in an alcohol extract of liver, of an acidic ether-extractable substance essential for the normal growth of 14 species of lactic acid bacteria. This substance

is rather labile to heat, acid, and especially to alkali, is adsorbed by charcoal but not by Lloyd's reagent, and is not precipitated by phosphotungstic acid.

As work has progressed on the activator requirements of the betacocci, communications describing the nature of the essential dietary factors of the heat-stable portion of the Vitamin-B complex required for the growth of the rat and of the chick have appeared from other laboratories. A detailed summary of the properties of the constituents of the Vitamin-B complex is to be found in the paper by Edgar and Macrae (6).

Edgar and Macrae (4, 5, 6) describe the separation from autoclaved yeast extract of two heat-stable factors necessary for the optimum growth of rats maintained on a Vitamin B-free diet and receiving lactoflavin and Vitamin B_1. One factor is present in the filtrate after exhaustive extraction with fuller's earth, while the second is contained in the eluate from the fuller's earth adsorbate after the removal of lactoflavin. The fuller's earth filtrate factor is adsorbed by Norite charcoal at pH 1.2 and is not precipitated by phosphotungstic acid.

Elvehjem and Koehn (7) first described a fuller's earth filtrate factor present in an aqueous liver extract and necessary for the growth of the chick. This factor was later investigated by Lepkovsky and Jukes (9). Unlike the yeast filtrate factor of Edgar and Macrae, the liver filtrate factor is not adsorbed by Norite charcoal.

The yeast fuller's earth adsorbate factor may be similar to, or identical with, the factor obtained by Lepkovsky and co-workers (10) from the fuller's earth adsorbate from rice bran extracts. In certain respects Edgar and Macrae's adsorbate factor resembles the Vitamin B_6 investigated by Birch and György (1). Edgar and Macrae, and Lepkovsky and co-workers do not describe the properties of their respective adsorbate factors, in so far as their adsorption by charcoal or precipitation by phosphotungstic acid are concerned. Vitamin B_6 is adsorbed by fuller's earth at pH 2.5, but not by charcoal at pH 6.0, and is precipitated by phosphotungstic acid.

A review of the literature on the question of the relation of Bios to the Vitamin-B complex shows that the evidence is overwhelmingly against the suggested identity of Bios and Vitamin B_1. In their early work on the fractionation of Bios, Miller and co-workers (2,11) showed that neither Bios I nor Bios II (adsorbed by charcoal) cured avian polyneuritis or promoted the growth of rats. However, in the light of the more recent work on the multiple nature of the Bios factors required for the growth of yeasts (12, 18, 19), and of the demonstration of several heat-stable dietary factors essential for the nutrition of the rat, it appeared not improbable to assume that a relation might exist between the Bios factors and certain of the B-vitamins. A study of the chemical and physical properties of the factors constituting the Bios of Wildiers and the Vitamin-B complex strongly suggested to us that the Bios activators, which we have shown are required by the lactic acid bacteria for their most intensive metabolism, are identical with certain of the heat-stable components of the Vitamin-B complex.

In an attempt to establish the validity of the writers' hypotheses, fractionation of tomato juice, by means of a combination of the procedures used for the differentiation of the Bios constituents and for the characterization of the heat-stable components of the Vitamin-B complex, was undertaken. The behavior of the respective entities towards adsorption by charcoal and by fuller's earth, and towards precipitation by phosphotungstic acid, was used as a basis for separation.

Experimental

The filtrate resulting from the treatment of the contents of two tins of tomato juice with tannic acid and lead acetate, with subsequent removal of hydrogen sulphide, was used as the starting material for the preparation of the various fractions (12).   This filtrate was divided into two equal portions, Filtrates 1 and 2.

Filtrate 1 was treated after the manner of Miller (12) for the separation of Bios II *A* and Bios II *B*.   These Bios preparations were concentrated to 100 cc. and 50 cc. quantities respectively.   A fuller's earth filtrate factor and a fuller's earth adsorbate factor were prepared from Filtrate 2 after the manner of Edgar and Macrae.   These vitamin factors were also concentrated to 100 cc. and 50 cc. quantities respectively.   An aliquot equivalent to one-fifth of the volume of each of the Bios and vitamin concentrates was retained for the purpose of determining its influence on the acid-producing abilities of the lactic acid micro-organisms.

Fuller's earth filtrate and adsorbate fractions were prepared by the procedure of Edgar and Macrae from the remainder of each of the Bios concentrates after they had been made up to a volume of 600 cc.   Each of the resulting fractions was concentrated to the volume of the solution from which it was prepared.

The four fractions thus obtained were:—

> Fuller's earth filtrate of Bios II *A*—   Fraction 1
> Fuller's earth adsorbate of Bios II *A*—   Fraction 2
> Fuller's earth filtrate of Bios II *B*—   Fraction 3
> Fuller's earth adsorbate of Bios II *B*—   Fraction 4

Charcoal adsorbate and filtrate fractions were prepared by the procedure of Miller from the remainder of the fuller's earth filtrate and fuller's earth adsorbate factors.   Each solution was made up to a volume of 600 cc. prior to treatment with charcoal, and each of the resulting fractions was concentrated to the volume of the solution from which it was prepared.

The four fractions thus obtained were:—

> Charcoal filtrate of fuller's earth filtrate—   Fraction 5
> Charcoal adsorbate of fuller's earth filtrate—   Fraction 6
> Charcoal filtrate of fuller's earth adsorbate—   Fraction 7
> Charcoal adsorbate of fuller's earth adsorbate— Fraction 8

An aliquot equivalent to one-quarter of the volume of each of the eight fractions was retained for the purpose of determining its influence on the acid-producing ability of the lactic acid micro-organisms.

A phosphotungstic acid precipitation was carried out on the remainder of each of the eight fractions. Each fraction was diluted to a volume of 200 cc., adjusted to contain 5% of sulphuric acid by volume, and precipitation was effected with 20% phosphotungstic acid in 5% sulphuric acid. The phosphotungstic acid precipitates and filtrates were freed from phosphotungstic acid in the usual manner, and each of the resulting solutions was concentrated to the volume of the solution from which it was prepared. Fraction 3 failed to yield a phosphotungstic acid precipitate.

The influence of each of the preparations, when added to milk as an enriching entity, on the acid-producing abilities of cultures EMB_1173 and

TABLE I

TITRATABLE ACIDITY IN GRAMS LACTIC ACID PER LITRE

Medium employed as substrate	Culture number	
	EMB_1173	EMB_2173
Milk	3.6	1.6
Milk + 0.15% yeast extract	6.5	3.4
Milk + Bios II A	7.4	7.4
Milk + Fraction 1	7.2	6.3
Milk + PTA* precipitate of Fraction 1	3.6	1.8
Milk + PTA filtrate of Fraction 1	4.5	4.7
Milk + Fraction 2	3.6	1.8
Milk + PTA precipitate of Fraction 2	3.6	1.6
Milk + PTA filtrate of Fraction 2	3.6	1.6
Milk + Bios II B	5.4	3.6
Milk + Fraction 3	4.7	3.6
Milk + PTA precipitate of Fraction 3	—	—
Milk + PTA filtrate of Fraction 3	3.4	1.6
Milk + Fraction 4	6.3	3.2
Milk + PTA precipitate of Fraction 4	5.6	2.7
Milk + PTA filtrate of Fraction 4	3.6	1.6
Milk + Fuller's earth filtrate factor	6.8	3.6
Milk + Fraction 5	5.6	4.1
Milk + PTA precipitate of Fraction 5	3.6	1.6
Milk + PTA filtrate of Fraction 5	5.9	4.7
Milk + Fraction 6	5.9	2.7
Milk + PTA precipitate of Fraction 6	4.3	1.6
Milk + PTA filtrate of Fraction 6	6.1	1.8
Milk + Fuller's earth adsorbate factor	5.2	2.9
Milk + Fraction 7	3.2	1.1
Milk + PTA precipitate of Fraction 7	3.6	1.6
Milk + PTA filtrate of Fraction 7	4.3	1.6
Milk + Fraction 8	5.4	3.4
Milk + PTA precipitate of Fraction 8	5.9	2.9
Milk + PTA filtrate of Fraction 8	3.6	2.0

* PTA *stands for phosphotungstic acid.*

EMB$_2$173 (15, 16) was determined. The enrichment was added at the rate of 1% in all cases. Milk and milk enriched with 0.15% autolyzed yeast extract served as controls. Culture EMB$_1$173 is an atypical strain of *Streptococcus cremoris* (Orla-Jensen) responding markedly to the enrichment of milk with yeast extract. Culture EMB$_2$173 is to be classified as a strain of *Betacoccus cremoris* (Knudsen and Sørensen). Procedures followed throughout the fermentation study have been described previously (15). The results of the determinations of the total titratable acidity produced by each of the cultures are given in Table I.

When the data for the acid production of cultures EMB$_1$173 and EMB$_2$173 are considered, it is obvious that enrichment of milk with either Bios II *A* or Bios II *B* has a marked stimulating effect on the vital activity of the micro-organisms, and that the influence of Bios II *A*, particularly in the case of culture EMB$_2$173, is more marked than that of Bios II *B*, previous results being thus confirmed (3) (Table I).

The addition of the fuller's earth filtrate factor or of the fuller's earth adsorbate factor has a marked stimulating effect on the vital activity of both micro-organisms. The total titratable acidity produced by culture EMB$_1$173 in milk enriched with the fuller's earth filtrate factor is equal to that produced when Bios II *A* is employed as the enriching entity. It would appear that culture EMB$_2$173 is stimulated to a greater extent by Bios II *A* than by the fuller's earth filtrate factor. It is difficult at this time to provide an adequate explanation of this phenomenon; it is possible, however, that the sensitivity of the organism to varying concentrations of the active principles accounts for the apparent discrepancy observed in the stimulating abilities of accessory factors, which resemble each other in many respects. The activation produced by enrichment of milk with the fuller's earth adsorbate factor is practically identical with that obtained by the addition of Bios II *B* in the case of both micro-organisms.

A study of the influence of the eight fractions prepared from Bios II *A*, Bios II *B*, the fuller's earth filtrate factor, and the fuller's earth adsorbate factor on the activity of the micro-organisms shows clearly that a relation exists between the Bios constituents and the heat-stable components of the Vitamin-B complex.

On the basis of the adsorption reactions employed for the preparation of these fractions, a close resemblance in the acid-stimulating abilities of Fractions 1 and 5, 2 and 7, 3 and 6, 4 and 8, respectively, is to be expected. The results detailed in Table I bear out this expectation. It is evident that we are dealing with only four distinct fractions. The fractions that are adsorbed by fuller's earth but not by charcoal, Fractions 2 and 7, are inactive. Marked stimulating ability is to be found, however, in all other fractions. It is apparent that we are concerned with three distinct activating entities: a factor adsorbed by charcoal and by fuller's earth, Fractions 4 and 8; a factor adsorbed by charcoal but not by fuller's earth, Fractions 3 and 6; and a factor that is not adsorbed by either charcoal or fuller's earth, Fractions 1 and 5.

Confirmation of these results was obtained when the solutions resulting from the treatment of the respective active fractions with phosphotungstic acid were employed as enriching entities. Of the active factors, only the one adsorbed by both fuller's earth and charcoal is precipitated by phosphotungstic acid.   Regardless of the order in which the adsorbents are employed for the separation of the respective fractions, corresponding pairs of factors react similarly in so far as their precipitability by phosphotungstic acid is concerned.   Although neither of the factors that are adsorbed by charcoal but not by fuller's earth is precipitated by phosphotungstic acid, a difference in the behavior of the respective solutions containing this factor towards phosphotungstic acid was observed.   Fraction 3, which was prepared by adsorption on charcoal prior to treatment with fuller's earth, yielded no precipitate, and the factor became inactivated by the addition of phosphotungstic acid.   Fraction 7, on the other hand, yielded a phosphotungstic acid precipitate, the filtrate retaining the stimulating activity of the fraction.

Fractionation of Bios II *A* yielded two fractions, only one of which was active, Fraction 1.   Fraction 5, obtained from the fuller's earth filtrate factor, exhibited similar chemical, physical, and biological characteristics. On the basis of its chemical and physical properties, the Bios II *A* of Miller would appear to be identical with the liver filtrate factor described by Elvehjem and Koehn, and Lepkovsky and Jukes.

Treatment of Bios II *B* with fuller's earth yields two active components, Fractions 3 and 4, a filtrate factor not precipitable by phosphotungstic acid, and an adsorbate factor precipitable by this reagent.   Fraction 6, obtained from the fuller's earth filtrate factor, was similar to Fraction 3.   Fraction 8, the fraction adsorbed by charcoal from the fuller's earth adsorbate factor, resembled Fraction 4.

The activating constituent of Bios II *B* not adsorbed by fuller's earth is similar to the fuller's earth filtrate factor described by Edgar and Macrae.

From a study of the properties of the other active component of Bios II *B*, adsorbed by fuller's earth and precipitated by phosphotungstic acid, it would appear that this activator is distinct from any of the dietary factors of the Vitamin-B complex described by various workers.   It resembles in certain respects the Vitamin B_6 of Birch and György and the factor obtained from rice bran extracts by Lepkovsky and co-workers.   Unlike Vitamin B_6, this component of Bios II *B* is adsorbed by Norite charcoal even at pH 6.

To establish more clearly the relation between the Bios factors and the constituents of the Vitamin-B complex, fractionation of liver and yeast extracts, the principal materials used as sources of the B-vitamins, was undertaken.

When an aqueous extract of either of these materials, autoclaved for five hours at 120° C., was fractionated, the stimulating abilities of the resulting activators were found to be similar to those of corresponding entities prepared from canned tomato juice.   Thus, canned tomato juice, autoclaved yeast

extract, or autoclaved liver extract may serve as sources of the three distinct activators.

In an attempt to obtain further evidence supporting the hypothesis that two of the three activators required by the lactic acid bacteria are similar to the factors described by Edgar and Macrae, fractionation of an autoclaved extract of brewers' yeast was carried out, the method described by these workers being followed in strict detail. In their procedure, adsorption with fuller's earth is carried out directly on an acid extract of the material, without an intervening tannic acid and lead acetate precipitation. Fractions corresponding to their fuller's earth adsorbate and filtrate factors were prepared.

The filtrate remaining after successive treatment with fuller's earth and charcoal should contain the Bios II A entity. This filtrate did exhibit slight stimulating ability, which however did not approach that exhibited by Fractions 1 and 5, obtained when the procedure of Miller, using a tannic acid and a lead acetate precipitation, was employed. It would appear that in the procedure of Edgar and Macrae this factor may be partially removed by treatment with fuller's earth. Although we have not carried out tests on the activity of the washings of the fuller's earth prior to elution, it is possible that the II A factor may be found therein. Of the two factors described by Edgar and Macrae, one is adsorbed by charcoal and the other by both charcoal and fuller's earth. It is to be noted that Edgar and Macrae do not describe a factor possessing the properties of Fractions 1 and 5. As shown above, each of these fractions is identical with Bios II A and the liver filtrate factor of Elvehjem and Koehn, and is not to be found in appreciable quantities in the filtrate after treatment of an activated yeast extract with fuller's earth and charcoal after the manner of Edgar and Macrae.

If the Bios II B fraction, which contains the two factors described by Edgar and Macrae, was prepared from an unautoclaved extract of brewers' yeast, it was found to exert only a slight influence on the acid-producing abilities of the micro-organisms. Subsequent autoclaving of this fraction, however, resulted in an increased activity approximating the activity possessed by the Bios II B prepared from an extract of yeast autoclaved prior to fractionation.

The three activators were also separated from an autoclaved extract of fresh hog's liver, by use of the procedures employed in the fractionation of brewers' yeast. No Bios II A activity was obtained when direct adsorption with fuller's earth and charcoal was employed. Unless the liver extract was autoclaved prior to fractionation, the Bios II B fraction possessed only slight stimulating activity.

On consideration of the results as a whole, it is evident that three distinct growth stimulants other than Bios I (inositol) are present in tomato juice, autoclaved yeast extract, and in autoclaved liver extract, and that these activators are essential for the most intensive metabolism of certain lactic acid bacteria. One of these activators is Bios II A, and the other two have been shown to be components constituting Bios II B.

Although it has been impossible to carry out confirmatory biological testing of the factors on laboratory animals, the nature of the physical and chemical characteristics of the activators, combined with the results obtained when lactic acid micro-organisms have been used as an index of the activating power of the entities, strongly suggests that these factors required by the lactic acid bacteria are identical with certain of the heat-stable accessory food factors of the Vitamin-*B* complex.

References

1. BIRCH, T. W. and GYÖRGY, P. Biochem. J. 30 : 304-315. 1936.
2. DEAS, J. J. Biol. Chem. 61 : 5-8. 1924.
3. EAGLES, B. A., WOOD, A. J., and BOWEN, J. F. Can. J. Research, B, 14 : 151-154. 1936.
4. EDGAR, C. E., MACRAE, T. F., and VIVANCO, F. Biochem. J. 31 : 879-885. 1937.
5. EDGAR, C. E. and MACRAE, T. F. Biochem. J. 31 : 886-892. 1937.
6. EDGAR, C. E. and MACRAE, T. F. Biochem. J. 31 : 893-902. 1937.
7. ELVEHJEM, C. A. and KOEHN, C. J. J. Biol. Chem. 108 : 709-728. 1935.
8. GYÖRGY, P. Biochem. J. 29 : 741-759. 1935.
9. LEPKOVSKY, S. and JUKES, T. H. J. Biol. Chem. 114 : 109-116. 1936.
10. LEPKOVSKY, S., JUKES, T. H., and KRAUSE, M. E. J. Biol. Chem. 115 : 557-566. 1936.
11. LUCAS, G. H. W. J. Phys. Chem. 28 : 1180-1200. 1924.
12. MILLER, W. L. Trans. Roy. Soc. Canada, 30, III : 99-103. 1936.
13. MILLER, W. L., EASTCOTT, E. V., and MACONACHIE, J. E. J. Am. Chem. Soc. 55 : 1502-1517. 1933.
14. ORLA-JENSEN, S., OTTE, N. C., and SNOG-KJAER, A. The vitamin and nitrogen requirements of the lactic acid bacteria. D. Kgl. Danske Vidensk. Selsk. Skrifter, Naturv. og Math. Afd., 9, Raekke, VI. 6. Copehagen. 1936.
15. SADLER, W., EAGLES, B. A., and PENDRAY, G. Can. J. Research, 7 : 370-377. 1932.
16. SADLER, W., EAGLES, B. A., BOWEN, J. F., and WOOD, A. J. Can. J. Research, B, 14 : 139-150. 1936.
17. SNELL, E. E., STRONG, F. M., and PETERSON, W. H. Biochem. J. 31 : 1789-1799. 1937.
18. WILLIAMS, R. J., WILSON, J. L., and AHE, F. H. V. DER. J. Am. Chem. Soc. 49 : 227-235. 1927.
19. WILLIAMS, R. J. and BRADWAY, E. M. J. Am. Chem. Soc. 53 : 783-789. 1931.
20. WILLIAMS, R. J. and SAUNDERS, D. H. Biochem. J. 28 : 1887-1893. 1934.

STUDIES ON LIGNIN AND RELATED COMPOUNDS

XXXIII. ISOLATION OF ACETOVANILLONE FROM WASTE SULPHITE PULP LIQUOR[1]

By IRENE K. BUCKLAND[2], GEORGE H. TOMLINSON II[3] AND HAROLD HIBBERT[4]

Abstract

Waste sulphite pulp liquor (obtained in the manufacture of a commercial sulphite pulp from soft woods, principally spruce and balsam) on treatment with aqueous alkali gave vanillin, acetovanillone, phenolic substances, and a tarry resinous product. The yield of acetovanillone is about 5.5% of that of the vanillin formed, or about 0.3% calculated on the basis of the lignin present.

Introduction

In a previous note (3) announcement was made of the discovery that small quantities of acetovanillone can be obtained from waste sulphite pulp liquor (from soft wood). In the present communication a description is given of the isolation of this compound, and its identification with the pure synthetic product.

A commercial waste sulphite pulp liquor on similar treatment yielded, in addition to vanillin, a viscous oil, which, after treatment, was found to contain *(a)* phenolic substances, *(b)* a crystalline solid, and *(c)* a residual tar, in yields of 3.2, 5.5, and 49.5%, respectively, of the weight of the vanillin found.

The crystalline solid, after suitable purification, was shown to be acetovanillone, identical in all its physical and chemical properties with the pure synthetic product.

The phenolic substances and the tarry residue are being investigated.

The fact that acetovanillone gives no precipitate with *m*-nitrobenzoyl hydrazine proves that its presence does not interfere with the estimation of vanillin by means of this reagent (6).

Experimental

Waste sulphite liquor* (114 litres), obtained in the commercial manufacture of a sulphite pulp from soft woods (principally spruce and balsam), was heated with sodium hydroxide under pressure, and the vanillin (297.5 gm.) extracted from the reaction mixture with benzene, the procedure previously outlined for the small-scale preparation (6) being followed. Removal of the

solvent left 178.3 gm. of a dark viscous oil, which was distilled under reduced pressure.   Three fractions were isolated.   Fraction 1 (9.7 gm.) was a mixture of phenolic substances, b.p. 56° to 86° C. at 5.2 mm. initial pressure—diminishing to 1 mm. as the distillation proceeded; Fraction 2, b.p. 140° to 160° C. at 2 mm., bath temperature 230° C., crystalline solid (16.4 gm.); Fraction 3, residual tar (147.2 gm.).

Identification of the Crystalline Product (Fraction 2)

This was redistilled and gave two fractions: *(a)* a mixture of an oil with a crystalline solid (1.0 gm.), b.p. 60° to 80° C. at 2 mm.; *(b)* a white crystalline solid as principal fraction, b.p. 157° to 180° C. at 1.7 mm.   On recrystallization of the latter product from benzene it was obtained in the form of broad colorless leaflets, m.p. 114.5° C.; OCH$_3$, 18.7, 18.6%.   Calcd. for acetovanillone: (C$_9$H$_{10}$O$_3$): OCH$_3$, 18.68%.

The semicarbazone was prepared from semicarbazide hydrochloride and sodium acetate in alcohol solution (50%); m.p. 165.5° to 166° C.

Identity of the Crystalline Product with Synthetic Acetovanillone

Attempts to prepare acetovanillone from guaiacol acetate by treatment with anhydrous aluminium chloride (4) were unsuccessful, the acetate being recovered unchanged.   A similar result was found by Barch (2), who, however, by using the modified procedure of Baltzly and Bass (1), showed that the Fries rearrangement could be carried out in nitrobenzene as solvent.

Method

A solution of aluminium chloride (34 gm.) in 125 gm. of nitrobenzene was added, with stirring, to 25 gm. of guaiacol acetate; the mixture was then cooled to 0° C. and stirred for 20 hr. at room temperature.   The orange-red reaction mixture was poured on cracked ice, and then extracted with three volumes of ether.   The extract was neutralized by shaking with aqueous bicarbonate.   The ether was evaporated off and the residue distilled under diminished pressure.   The nitrobenzene and guaiacol acetate distilled over at 77° to 81° C. at 2.2 to 1.0 mm., and then 12 gm. of an oily solid at 132° to 140° C. at 1.0 mm.   The latter fraction was purified by recrystallization from benzene and obtained in the form of fine white needles; yield, 6.0 gm. m.p. 115° C.; (m.p. reported (5) 115° C.).

A mixture of this and the acetovanillone obtained from waste sulphite pulp liquor showed no lowering in melting point (114° to 115° C.).

The semicarbazone of the synthetic acetovanillone was prepared in the manner described above; m.p., 164.5° to 165.5° C.; mixed melting point with previous preparation, 164.5° to 165.5° C.

Reaction with Ferric Chloride

Both preparations of acetovanillone (synthetic, and that from waste sulphite pulp liquor) gave the same typical reaction with ferric chloride; namely, a blue coloration which disappeared on heating, owing to precipitation of dehydro-diacetovanillone.

Attempted Preparation of m-Nitrobenzoyl Hydrazone of Acetovanillone

Acetovanillone was found to give no precipitate with *m*-nitrobenzoyl hydrazine (such as is obtained with vanillin) by the method described previously (6).

References

1. BALTZLY, R. and BASS, A.,   J. Am. Chem. Soc. 55 : 4292-4294.   1933.

2. BARCH, W. E.   J. Am. Chem. Soc. 57 : 2330.   1935.

3. BUCKLAND, I. K., TOMLINSON, G. H. and HIBBERT, H.   J. Am. Chem. Soc. 59 : 597. 1937.

4. MOTTERN, H.   J. Am. Chem. Soc. 56 : 2107-2108.   1934.

5. TIEMANN, F.   Ber. 24: 2855–2862.   1891.

6. TOMLINSON, G. H. and HIBBERT, H.   J. Am. Chem. Soc. 58 : 345-353.   1936.

AN ALKALOID FROM *DELPHINIUM BROWNII* RYDB.[1]

By RICHARD H. F. MANSKE[2]

Abstract

Delphinium brownii contains a total of 0.5% of alkaloids, hydrolysis of which yields a crystalline base, probably $C_{22}H_{37}O_7N$ or $C_{23}H_{39}O_7N$, together with anthranilic and methylsuccinic acids. Mannitol is present in considerable amounts.

The chemistry of the *Delphinium* alkaloids, even more so than that of the *Aconitum* alkaloids, is still in the earliest stages of development. Though both classes have been known for many years, little knowledge of the constitution of even a single individual is available. The classical methods employed for the structural study of many other alkaloids fail entirely, or yield results which at present are not susceptible of satisfactory interpretation. The nature of the functional groups in aconitine appears now to have been established (1) although the carbon skeleton remains to be determined.

Most of the positive results in the chemistry of these alkaloids, which, because of their closely related botanical origin may be considered chemically similar, are confined to hydrolytic cleavage, identification of the acid fragments, and characterization of the basic moiety. Benzoic and acetic acids are commonly obtained. Several of the aconite alkaloids have yielded anthranilic acid which itself is combined with succinic acid in the form of an anil (3).

The alkaloid now obtained from *Delphinium brownii* Rydb. belongs to the anthranilic type, in that hydrolysis yields anthranilic acid. Instead of succinic acid, however, the corresponding anil is derived from methylsuccinic acid, and this appears to be the first isolation of the latter from natural sources. It may be pertinent to point out that methylsuccinic acid contains the isoprene carbon skeleton which is also present in tiglic and angelic acids, $\beta\beta$-dimethylacrylic acid (senecioic acid), and reductic acid, all of which occur naturally. The hypothesis that the *Delphinium* and *Aconitum* alkaloids are isoprene derivatives is an attractive one. However, selenium dehydrogenation, which has been so conspicuously successful with terpenes and steroids, is of less utility with nitrogenous bases.

The main alkaloid of *Delphinium brownii* Rydb., for which no name is as yet proposed, has not been obtained crystalline. Combination with a number of acids which include hydrochloric, sulphuric, acetic, oxalic, nitric, perchloric, and phosphoric has likewise failed to yield a crystalline product. Hydrolysis with methanolic potassium hydroxide yields, in addition to the organic acids already mentioned, a well crystallized base, which was also isolated without intentional hydrolysis from the crude alkaloid. No ultimate proof of the homogeneity of the hydrolytic base is available. Nevertheless, its repeated preparation and apparently identical properties when

different lots of plant material were examined can scarcely be coincidental. Analytical figures are intermediate between those for $C_{22}H_{37}O_7N$ and $C_{23}H_{39}O_7N$, and the presence of three or four methoxyl groups is indicated. Molecular weight determinations indicate a smaller molecule, and $C_{20}H_{33}O_6N$ containing three methoxyls is not entirely excluded. An attempt to obtain a benzoyl derivative yielded an amorphous product, and a decision as to the correct formula must await further work.

Finally, it may be mentioned that *D. brownii*, like many other *Delphinium* species (2), contains a relatively large amount of mannitol.

Experimental

Isolation of the Total Alkaloids

The plant was collected in southern Alberta, where it grows wild. The dried and ground aerial portion was extracted with methanol and the solvent removed from the extract. Water was added and sufficient hydrochloric acid to insure acidity to Congo red. The mixture was heated on a steam bath to coagulate the fats and resin, and then cooled. In general it was then possible to decant the clear aqueous solution from the insoluble portion. (It is convenient to work with such dilutions that a litre of final extract is prepared from 1 to 2 kilos of plant material.) The aqueous solution was filtered with a little charcoal and extracted several times with ether (LC). It was then basified with excess ammonium hydroxide and extracted with ether until no more extract was obtained. In some experiments a small amount of the total base crystallized from the concentrated ether extract. This proved to be identical with the hydrolytic base described later. It was difficult to purify, and the author is greatly indebted to Dr. E. H. Charlesworth for carrying out this purification and identification.

The crude total alkaloid was dissolved in dilute oxalic acid and the filtered solution repeatedly extracted with ether. When this solution was basified with potassium hydroxide and the base again extracted with large volumes of ether, a pale colored alkaloid containing virtually no neutral material was obtained. The yield by this procedure was 0.50%.

In an earlier attempt to obtain a single individual in a crystalline condition, an ethereal solution containing 40 gm. of total alkaloid was fractionally extracted with six successive equal portions of dilute hydrochloric acid, and the base regenerated from each extract. The last two were combined, and thus five fractions of alkaloid were obtained. No crystalline material was obtainable from any of these fractions. Hydrolysis with alkali yielded in each case approximately the same amount of crystalline hydrolytic base.

Isolation of Mannitol

The ammoniacal solution from which the crude alkaloid had been extracted was filtered and evaporated *in vacuo* to a thick syrup. This was extracted with successive portions of hot methanol, and the extracts were evaporated

to a thin syrup. After several days the crystalline product which had separated was filtered off. It was then recrystallized from dilute methanol, 95% ethanol, and water in the order named. It then melted at 166° C.* either alone or in admixture with an authentic specimen. The author takes this opportunity to note that the same carbohydrate alcohol has been found in relatively large amounts in *Lactarius deceptivus* Pk. The estimated total amount of mannitol in the *Delphinium* is about 1.5%.

Hydrolysis of the Alkaloid

A solution of the purified alkaloid in methanol was treated with twice its weight of potassium hydroxide in 50% aqueous solution. It was heated on a steam bath for 12 hr., diluted with water, and the methanol evaporated. During the last-mentioned process the crude hydrolytic base gradually crystallized. After cooling, the mixture was filtered and washed with water and ether alternately. There remained a colorless crystalline residue which was further purified by recrystallizing from ether in a Soxhlet extractor. Final purification was effected by dissolving a portion in dilute methanol and adding hot water and a nucleus to the filtered solution. As thus obtained, this base melts at 120° to 121° C., some sintering taking place several degrees lower. For analysis the substance was dried in a high vacuum over phosphorus pentoxide for 24 hr. Found: C, 62.12, 62.14; H, 8.62, 8.86; N, 3.30; 3.22; OMe, 26.10, 29.26, 23.51, 25.23%. M.W. 307, 315 (Rast). Calcd. for $C_{22}H_{37}O_7N$: C, 61.82; H, 8.67; N, 3.28; 3 OMe, 22.81%. The optical activity of $[\alpha]_D^{22} = +52.2°$ ($c = 0.8$ in methanol) points to a similarity to, if not identity with, lycoctonine (3).

The ether washings from the crude base deposited a small amount of crystalline material on long standing, and a further small amount was obtained by repeating the hydrolysis. There remained a not inappreciable amount of virtually colorless resinous base, the examination of which is still in progress.

Isolation of Anthranilic and Methylsuccinic Acids

The aqueous alkaline filtrate from the preparation of the above-mentioned crystalline base was rendered just acid with hydrochloric acid and filtered from a small amount of amorphous precipitate. It was repeatedly extracted with ether, and the combined extracts were evaporated to a small volume. The crystalline product thus obtained was filtered off and recrystallized three times from hot water. It melted at 145° C. and this melting point was not depressed when the substance was admixed with a specimen of anthranilic acid. Esterification with methanol yielded the characteristic odor of synthetic grape flavor. Calcd. for $C_7H_7O_2N$; C, 61.31; H, 5.11; N, 10.22%. Found: C, 61.27; H, 5.13; N, 10.40%.

The filtrate from the crude anthranilic acid was evaporated to dryness and the residue recrystallized twice from dry ether. It was obtained in colorless fine prisms which melted at 112° C. and showed no optical activity

* *All melting points are corrected.*

in water ($c = 0.8$). When it was admixed with a specimen of synthetic methylsuccinic acid melting at 114° C., there was no observable depression in melting point. It gave the characteristic fluorescine test with great brilliance when heated with resorcinol and sulphuric acid. Calcd. for $C_5H_8O_4$; C, 45.46; H, 6.06%. Found: C, 45.67; H, 6.18%.

No indication of the presence of acetic, benzoic, or other acids was obtained in any of the hydrolysis experiments.

References

1. FREUDENBERG, W.   Ber. 69 : 1962-1965.   1936.
2. JARETZKY, R. and SCHAUB, C.   Arch. Pharm. 271 : 171-174.   1933.
3. SCHULZE, H. and BIERLING, E.   Arch. Pharm. 251 : 8-49.   1913.

A NEW METHOD FOR THE DETERMINATION OF VARIOUS FIBRES IN MIXTURES, WITH SPECIAL REFERENCE TO THE DETERMINATION OF LANITAL IN WOOL-LANITAL MIXTURES[1]

By P. Larose[2]

Abstract

The method of Da Schio (1) for the determination of lanital in lanital-wool mixtures has been tried and found to be unreliable. A new and satisfactory method has been developed. This method makes use of the difference in the specific gravities of wool and lanital to separate the fibres by means of a liquid of intermediate specific gravity. The Herzog-Skinkle method has been found to give results that are a little high. The method devised by the author is also applicable to wool-cotton and wool-staple rayon mixtures. Results of tests carried out on various mixtures and by various methods are given.

No special difficulties have been experienced in the determination of various types of fibres in mixtures. The fibres that were usually found together differed sufficiently in some chemical property to make a separation by chemical means possible, with a reasonable degree of success. However, with the introduction of lanital-wool* mixtures, a new problem presented itself; that of separating two fibres differing little in chemical properties. The difficulty is very similar to that encountered when the separation of cotton and viscose rayon was studied. It was found that differences in solubility in solutions of calcium thiocyanate gave a fairly good separation of the fibres. Da Schio proposed for the separation of lanital from wool a method based on the same principle, *i.e.*, the difference in rate of solubility of the two fibres in sodium hydroxide solutions.

The writer briefly reviewed Da Schio's method in a previous article (2) and pointed out its weakness. Further reference will be made to his method subsequently.

The problem was approached in a different manner by the writer, who tried to effect a separation by virtue of the difference in specific gravities of various fibres.

Following preliminary experiments which indicated that such a method would be feasible, determinations were made on two wool-lanital fabrics and on a wool-lanital top, which were the only samples available to the author. Unfortunately, all contained about equal quantities of lanital and wool, so that the method has not been given a fair trial with a wide variety of fabrics.

The principle of the method is such that its application is not limited to lanital-wool mixtures. With wool-cotton and wool-viscose rayon mixtures the method gave results that agreed well with those obtained with standard chemical methods, as the figures given later will show.

Da Schio's Method

In order to try out the method proposed by Da Schio, two mixtures were prepared from known quantities of pure wool and pure lanital. The first contained 66.8% of lanital by weight; the other, 38.1%.

The directions given by Da Schio were closely followed except as regards the temperature, which, inadvertently, was allowed to rise from 31° to 35° C. during the tests, and the results obtained were 59.3 and 34.7%, respectively, for the two mixtures, when the correction of 12.3% for the loss of lanital was made as required by Da Schio's method. However, the lanital blank, carried out simultaneously, gave a loss of 21.7%. If this figure is used in correcting for the loss of lanital, the calculated results are 66.4 and 38.9%, respectively, which show very good agreement with the actual amounts. It must be emphasized, nevertheless, that such agreement is possible only when a blank determination is made at the time that the samples are analyzed, and probably only when the same type of lanital as that present in the mixtures is used. These conditions obtained in the above-mentioned test. The difference between the 21.7% loss noted in the experiment and that of 12.3% given by Da Schio is due in part to the fact that the average temperature (33° C.) in this experiment was 2° higher than that recommended by Da Schio.

A wool-lanital top supposed to contain 50% of lanital was analyzed by this method, and at the same time a blank determination was made with some pure lanital tops obtained from the same source. The blank showed a loss in lanital of 9.2%, which gave a corrected figure of 49.3% of lanital in the mixed top.

A determination carried out subsequently on the pure lanital top treated in the same way showed a loss of 13.7%. The difference between this figure and the previous result of 9.2% may be due to some small change in the conditions of the experiments. These figures suffice to show the sensitivity of the method to small changes in the experimental conditions, and, no doubt, to differences between various lots of lanital.

The extreme precaution that has to be taken to obtain good results by this method makes it rather inconvenient for routine testing.

Separation Based on Differences in Specific Gravity
(Flotation Method)

Preliminary experiments indicated that although the difference in the specific gravities of lanital and wool is small, it is sufficient to enable a separation to be made by a flotation method. Lanital sinks in a liquid of specific gravity 1.300, but floats in one of specific gravity 1.310; wool floats in a liquid of specific gravity 1.320 but sinks in one of specific gravity 1.310. Consequently, if wool and lanital are present in a liquid of specific gravity 1.310, the lanital should float and the wool should sink, provided that the fibres are free to separate.

The success of the author's method depends largely upon the cutting of the yarn—the cut pieces should be as short as possible so as to permit easy

separation in the liquid. With the lanital-wool yarn investigated, the writer obtained good results with lengths of 1 mm. or less. The best length depends on the twist and the parallelism of the fibres of the yarn; the more twisted and the less parallel the fibres, the shorter they should be cut. Since the yarn tested had very little twist, the 1 mm. length probably represents the maximum length consistent with good results in the analysis of any yarn. The time of cutting is decreased considerably by holding several strands of the yarn together between the thumb and forefinger of the left hand and cutting them with sharp scissors, the bunch of yarns being pushed along as the cutting progresses.

When a sufficiently large sample of the cut ends has been obtained, it is transferred to the liquid adjusted to the correct specific gravity. The size of the sample may vary with the size of the vessel in which the separation is to be made. The writer found it best to use a large test tube, about 1 in. in diameter, and a sample weighing from 0.2 to 0.3 gm. The liquid used is a mixture of toluene and carbon tetrachloride. Other liquids could be employed, of course, but these two are very convenient as they are generally found in most laboratories.

The cut material is transferred to the test tube, and the liquid is added until the vessel is about three-quarters full. The tube is closed with a stopper, and the contents well shaken in order to separate the small bits of fibres. It is then left standing in an upright position and time allowed for the lanital to rise to the top and the wool fibres to sink. Two hours was generally found to be sufficient, although sometimes a longer period was required for proper separation to take place.

The tube is then opened and about half the liquid, carrying the floating lanital, is decanted into a filter paper in a funnel. Care must be taken during this operation not to agitate the tube so as to disturb the wool which has settled at the bottom. The remaining portion of the liquid with the wool is then poured on another filter paper. The separated fibres are then dried and weighed. The writer prefers weighing both portions of the separated fibres rather than weighing the original sample and then only one portion of separated fibres; the lanital, for example. If for any reason the separation fails, the operation of the original weighing is saved.

Since the regain of lanital is only slightly higher than that of wool, it is not necessary for practical purposes to weigh the fibres in the dry condition; it is sufficient to let them condition in the laboratory before weighing.

The success of the separation can be verified by examining some of the separated fibres under the microscope; any admixture of wool fibres with the lanital, or *vice versa*, is easily discerned. In general, the amount of one fibre mixed with the other was found to be small, but when it was fairly large each of the separated portions was treated in the same manner as the original sample, and in this way a complete separation was effected. The possibility of checking the complete separation of the fibres in this way is a decided advantage.

The small quantity of material necessary for the test is also an advantage when the sample available is small, although it may not be as representative of the whole fabric as a larger sample would be.   The method is so simple, however, and involves so little work that if a representative result is desired, several determinations can be made simultaneously with yarns taken from various parts of the cloth.

In the wool-lanital fabric tested by the writer, the variation along the yarn was fairly large, and several determinations had to be carried out to obtain a fair average value.   It seems that the spinning of wool-lanital yarn offers some difficulties, and that the technique is not yet such that a yarn of constant composition throughout its length can be spun.

In order to check the method, the correct percentage of lanital in the fabric had to be known.   To obtain this value, the writer had recourse to the tedious procedure of separating by hand the individual fibres in small samples and examining them under the microscope.   The separated fibres were weighed on a micro-balance.   It was found later that this separation could be made easier by dyeing the yarn with a dye such as Direct Sky Blue F.F.   This dyes the lanital fibres directly from a cold water solution, but the wool is hardly affected.   This is applicable, of course, only to light-colored fibres.   By examining against a dark background the fibres picked from the yarn, it was fairly easy with the naked eye to distinguish the lanital from the wool fibres.   The length of yarn used for the separation by means of the microscope was 3 in. while that employed in the separation of the dyed fibres by naked eye was 6 in.   The dyeing of the yarn, however, introduced a complication in the determination owing to the increase in weight of the lanital resulting from the addition of the dye.   A correction had to be made for this increase. This was determined by means of a blank test with a yarn weighed before and after dyeing.

Results

The first wool-lanital fabric on which most of the tests were performed was a checked material made from four colored yarns; yellow, white, grey, and brown in both warp and weft.   Reference has already been made to the variation in lanital content.   The following figures represent the percentage of lanital as determined by visual separation:

Yellow: warp, 51.8
          weft, 47.8, 46.8, 47.9, 46.9
Grey: warp, 51.6
          weft, 48.6, 43.2, 48.3
White: warp, 49.9
          weft, 50.8, 48.0, 52.0
Brown: warp, 48.5
          weft: 49.7, 42.7

Mean of all results, 48.4% lanital.

Owing to this high variation from sample to sample, it is difficult to judge, by comparison with these results, the accuracy of any one determination by the flotation method. However, as pointed out before, a microscopic examination of the separated fibres would show to what degree the separation had been successful, and hence would indicate roughly the degree of accuracy.

The following are the results obtained with the flotation method, the percentage of lanital being given:

Yellow: warp, 51.5, 53.5
            weft, 51.6, 48.0, 42.9
Grey: warp, 46.8
            weft, 46.8, 50.6, 44.1
White: warp, 50.2, 55.0, 44.9
            weft, 48.2, 50.8, 43.5, 47.2, 50.8
Brown: warp, 53.8, 49.0
            weft, 48.3

Mixed yarns: 47.2, 48.3

Mean of all results, 48.8% lanital.

The wool-lanital top that was used in testing Da Schio's method was also analyzed by the flotation method. Two determinations gave 49.3 and 48.2% of lanital, while a separation by visual means gave 48.9% of lanital.

A second lanital-wool fabric was analyzed. This was a small piece taken from an advertisement in a textile periodical. It was said to contain 50% of lanital and 50% of wool. The flotation method gave 50.8% of lanital. This determination was made with only 0.11 gm. of material.

A small sample, 0.13 gm., of this fabric, tested according to Da Schio's method, showed 45.7% of lanital when a loss of 12.3% was used as a blank correction, but 51.1% when 21.7% was the correction employed.

Determination of Lanital by the Herzog-Skinkle Method

Skinkle (3) used a modification of a method first proposed by Herzog for the determination of mohair in wool-mohair mixtures. In Herzog's method, in which the composition of the blend is determined by examining the fibres under a microscope and counting the number of each kind, use is made of the formula

$$\text{Percentage of Fibre } A = \frac{N_a G_a}{N_a G_a + N_b G_b} \times 100$$

where N_a is the number of fibres of constituent A,
    N_b is the number of fibres of constituent B,
    G_a is the weight of Fibres A per unit length,
    G_b is the weight of Fibres B per unit length.
The fibres are so cut that the average lengths of Fibres A and B are approximately the same.

Skinkle assumes that animal hairs are circular and that all have the same density. The weight per unit length would, therefore, be proportional to d^2, d being the diameter of the fibre. The formula then reduces to

$$\text{Percentage of Fibre } A = \frac{N_a d_a^2}{N_a d_a^2 + N_b d_b^2} \times 100 .$$

It is sufficient to count the number of fibres and to measure their mean diameter.

Since the apparent density of lanital differs from that of wool by only 1% or less, the error introduced in the percentage composition by assuming equal density would be, for a 1 : 1 mixture, about 0.25%, which, for all practical purposes, can be neglected.

The measurement of the diameter, on the other hand, has to be done very accurately to obtain good results.

In the fabric analyzed the mean diameter of the lanital fibres was found to be 22.2 μ, and that of the wool fibres, 20.6μ, these figures being the mean of those for 1100 fibres of each. An error of 0.2μ (which is not unreasonable) in the determination of the diameter would result in an error of 1% in the actual fibre content of the wool-lanital fabric tested.

Skinkle's method was applied to fibres cut in the same manner as those tested by the flotation method. It was assumed that, from the method of cutting, the average length of the wool fibres would be the same as that of the lanital fibres. Fourteen determinations were carried out on the various colored yarns and the same order of variation shown in the other methods was found. The mean of all determinations was 54.3% of lanital. If the difference in diameter was neglected and the percentage composition calculated from the number of fibres only, the value found for lanital was 51.0%. Similar results were obtained when $\frac{1}{4}$ in. sections of the yarn were cut, the fibres teased out, and counted under the microscope.

The method of cutting short lengths with two razor blades clamped together, as advocated by Skinkle, was also tried. The percentage of lanital found by counting fibres was 50.2%.

This method apparently gives, for the lanital in wool-lanital blends, results that are somewhat too high. This is perhaps due to the fact that the lanital fibres are not solid, but contain a number of cylindrical pores or canals which may be observed when the fibres are cross sectioned. The calculation of the percentage by means of Skinkle's formula is based on the supposition that the fibres are solid cylinders. If the lanital fibres are pierced by a series of longitudinal canals, the value used for the density in the transformation of Herzog's formula would have to be appreciably less than the true density of lanital.

Application of the Flotation Method to Other Blends

The application of the flotation method to the analysis of fibre mixtures other than wool-lanital is exemplified by the following results, which were obtained with two wool-staple rayon mixtures and two wool-cotton mixtures.

For the separation of the fibres in these mixtures, the toluene-carbon tetra-chloride solution was adjusted to a specific gravity (1.40) intermediate between that of wool and that of cotton or rayon.

The first wool-staple rayon yarn examined was from an automobile up-holstery fabric. Analysis of the fabric by chemical means (sulphuric acid method) gave a wool content of 45.8% in the warp and 42.9% in the weft, while the corresponding figures by the flotation method were 49.6 and 47.5%. The high results of the flotation method are largely due to the presence of small bits of the original highly twisted yarn mixed with the wool.

Better results were obtained with the other wool-viscose yarn which was from a dress material and not twisted to the same extent. The percentages of wool in this material as found by various methods are:

By chemical means (H_2SO_4 method):	38.2, 37.3; mean 37.8%
By chemical means ($Ca(CNS)_2$ method):	38.4, 37.9; mean 38.2%
Separation of fibres under microscope:	36.8, 36.2; mean 36.5%
By flotation:	35.6, 35.6, 36.0; mean 35.7%

A second sample of a similar fabric gave

By H_2SO_4 method:	36.1%
By $Ca(CNS)_2$ method:	35.5%
By flotation method:	36.0, 35.2, 36.0%.

The wool-cotton mixtures analyzed were both flannels. The first sample, tested by the sulphuric acid method, gave 46.5 and 45.6% of wool; mean, 46.1%. The flotation method gave 47.0, 47.3, and 46.9%; mean, 47.1%.

The second sample analyzed in the same way gave 61.2% of wool by the sulphuric acid method, and 60.6 and 62.4%, or a mean of 61.5%, by the flotation method.

The figures quoted are sufficient to show that the flotation method gives results that, on the whole, compare very favorably with those obtained by means of the ordinary chemical methods. It has the advantage of requiring less manipulation, and, moreover, it is possible to check the accuracy of the results by examination of the fibres under the microscope.

References

1. DA SCHIO, E. Boll. assoc. ital. chim. tessile color, 12 : 180. 1936.
2. LAROSE, P. Can. Textile J. 54, 15 : 32-33. 1937.
3. SKINKLE, J. H. Am. Dyestuff Reporter, 26 : 119-120. 1937.

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THE ISOLATION OF GUAIACOL FROM WASTE SULPHITE LIQUOR

Buckland, Tomlinson, and Hibbert (1, 2) have reported the isolation of acetovanillone from a waste sulphite liquor from soft woods; this has now been shown to be a degradation product of pure lignin sulphonic acid (3). In addition, a volatile phenolic, unidentified oil was obtained by them which has now been identified, by means of its boiling point and the *p*-nitrobenzoyl and *p*-toluene sulphonic esters, as guaiacol. The ratio of acetovanillone to guaiacol was approximately 4 : 1.

Investigation of a similar oil from lignin sulphonic acid from hard woods is in progress.

1. Buckland, I. K., Tomlinson, G. H., and Hibbert, H. J. Am. Chem. Soc. 59 : 597. 1937.
2. Buckland, I. K., Tomlinson, G. H., and Hibbert, H. Can. J. Research, B, 16 : 54-56. 1938.
3. Leger, F. J. and Hibbert, H. J. Am. Chem. Soc. 60 : March, 1938.

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THE CONVERSION OF FURFURYL ALCOHOL TO LEVULINIC ACID

Pummerer and co-workers (1, 2) have reported the conversion of furfuryl alcohol to methyl levulinate by the action of methanolic hydrochloric acid. Tchitchibabine (4, pp. 563-568) later confirmed the former authors' results.

The mechanism proposed for this conversion, involving the migration of a hydroxyl or methoxyl group from a 1 to a 5 carbon atom, this occurring either before or after ring opening, is clearly unsatisfactory. For this reason, a study of the reaction has been carried out in these laboratories.

The theory now proposed is similar to that offered by Scott and Johnson (3) for the conversion of furfuryl chloride to methyl pyromucic acid.

While addition of the elements of water is assumed in explaining the mechanism, those of methanol or mineral acid may actually be the ones which enter into the reaction. The first step involves 1 : 4 addition of the elements of water to the conjugated systems in furfuryl alcohol, followed by elimination in the carbinol and 2 position as shown (II).

(I)   (II)

(III)   (IV)
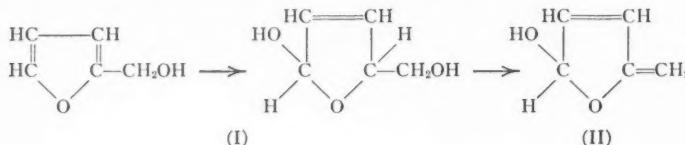
From II, through a 1,3 hydrogen migration and ketonization of the result-
ing enol, or migration of the conjugated system into the furane ring, α or
β angelica lactone (III and IV respectively) is formed.

By ring opening through addition of water, or by addition of the elements
of water to the double bond, the open chain or the ring form of levulinic
acid is formed from (III) or (IV).
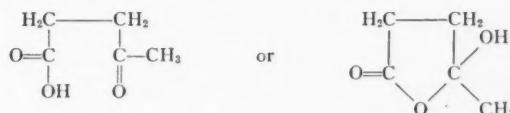
This same mechanism is also capable of explaining the formation of levulinic
acid from hydroxy methyl furfural, and of γ-keto pimelic acid from furyl
acrylic acid. It also serves to explain many other anomalies associated with
ring opening in the furane series.

Although the experimental proof of this mechanism is still somewhat in-
complete, evidence has been secured for most of the intermediate steps. It
is offered here since it appears that this conversion of furane derivatives
may have a definite bearing on the formation of lignin in the plant.

1. PUMMERER, R., BIRKHOFFER, L., and GUYOT, O. Ber. 68, B: 480-493. 1935.
2. PUMMERER, R. and GUMP, W. Ber. 56, B: 999-1008. 1923.
3. SCOTT, E. W. and JOHNSON, J. R. J. Am. Chem. Soc. 54 : 2549-2556. 1932.
4. TCHITCHIBABINE, A. E. Chimie et Industrie, Special No. March, 1932.

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MANUSCRIPT RECEIVED FEBRUARY 14, 1938.

THE STRUCTURE OF LIGNIN

In recent investigations on the structure of lignin there has been a marked
tendency to consider it either as derived from an oxyconiferyl aldehyde
(Freudenberg) or as originating from an unstable carbohydrate, the latter
undergoing a metamorphosis to lignin only during the process of extraction
from the plant (Hilpert).

Neither view is supported by adequate experimental evidence and it is
difficult to reconcile with such theories the recent discovery in these labora-
tories of guaiacol, vanillin, acetovanillone, syringic aldehyde, acetosyringone,

etc., as decomposition products of lignin sulphonic acids. On the other hand, these and numerous other reactions find a satisfactory explanation if the basic lignin building-constituent is viewed as arising from the condensation of guaiacol with fructose or one of its derivatives according to the following scheme:

Fructose

Hydroxymethylfurfuraldehyde   Fructuronic Acid

$$CH_2OH—CO—CH_2—CH_2—CO—CHO$$

$$CH_2OH—CO—CH_2—CH_2—CHO \quad (I)$$

$$CH_2OH$$

$$HO\langle\rangle—\overset{|}{C}—\quad HCOH—\langle\rangle OH \quad (II)$$
$$OCH_3 \quad OH \quad CH_2—CH_2 \qquad OCH_3$$

$$CH_2OH \qquad COOH$$

$$HO\langle\rangle—\overset{|}{C}—\quad HCOH—\langle\rangle OH \quad (III) \leftarrow$$
$$OCH_3 \quad OH \quad HCOH—HCOH \qquad OCH_3$$

$$\begin{array}{c} O \\ CH_2 \quad CO \\ HOCH \\ CO \quad HOCH \\ HCOH \end{array}$$

$$(IV) \quad CH_3—CO—CHOH—CHOH—CHO + CO_2$$

$$CH_3 \qquad OH$$

$$(V) \quad HO\langle\rangle—\overset{|}{C}—\quad H—\overset{|}{C}—\langle\rangle OH$$
$$OCH_3 \quad OH \quad HCOH—CHOH \qquad OCH_3$$
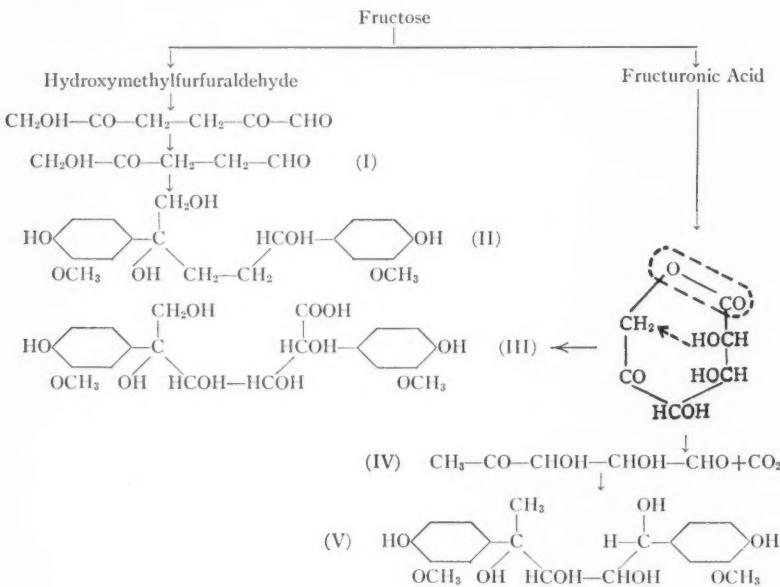
In the case of the furane intermediates derived directly from fructose, it is not necessary that the furane ring should actually open in the initial stages of the synthesis. As is indicated in the preceding note, intermediates VII and VIII might very well originate by addition of water to the hypothetical ring (VI), derived from furfuryl alcohol, followed by ring opening through addition of water.

$$\begin{array}{c} HO \quad CH══CH \\ \overset{|}{C} \quad C═CH_2 \quad (VI) \\ H \quad O \end{array}$$

$$CH_3—CO—CHOH—CH_2—CHO \qquad CH_3—CO—CH_2—CHOH—CHO$$
$$(VII) \qquad\qquad (VIII)$$
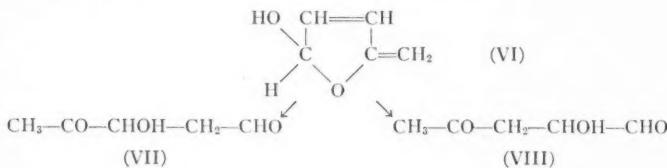
Each of these can then condense with one or two moles of guaiacol as shown above. Similarly the open-chain form of fructuronic acid can give rise to (III).

According to this "guaiacol theory of lignin formation", lignin represents essentially a condensation product of guaiacol with a 4-keto-oxy-pentanal

$$(-\overset{|}{\underset{|}{C}}-CO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{H}{\underset{}{C}}=O).$$
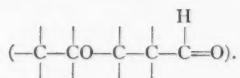
The many-sided character of the lignin complex, as will be shown in a forthcoming article, finds a satisfactory explanation when viewed from the above standpoint.   In hard woods, the guaiacyl- is partly replaced by the syringyl-radical.

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